

Project Description – Project Proposal for SPP 2171 (Erstantrag)

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1. State of the art and preliminary work

This project will study the dynamics of three-phase contact lines (3PCL) of droplets on surfaces. Experiments aim at inducing and analysing 3PCL movement on different dynamic substrates. Dynamic materials in this project include switchable materials, adaptive materials and flexible materials. Switchable materials will be represented by spiropyran-containing materials that can be either switched by light or by mechanical force. Spiropyran-containing photorheological gels with switchable softness represent the flexible materials and adaptive surfaces will be investigated by taking advantage of the acidic protonation of spiropyran surfaces, which results in a third molecular state of the spiropyran molecule with different surface energy properties. All processes shall be reversible and are thus in agreement with the prerequisites for research in this SPP. In the following a short overview will be given on the field of static and dynamic wetting on static and dynamic substrates to emphasize the importance of studying wetting phenomena on dynamic substrates. The integration into the Schwerpunktprogramm (SPP) will be discussed and underlined by the planned collaborations with other groups of the SPP.

Static wetting on static substrates

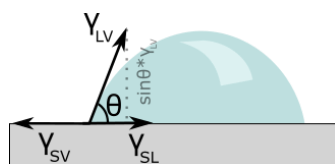


Figure 1: Young contact angle, defined by the surface energy of the liquid γ_{LV} , free surface energy of the solid γ_{SV} and the interfacial tension between solid and liquid γ_{SL} .

Wetting is defined as the spreading of a liquid on a surface. In wetting processes, the behaviour of liquids is to a large extent based on their surface tension, a force that, due to an energetic imbalance at the surface, drags the molecules located at the surface toward the bulk. Surface tension forces act towards keeping the individual molecules or atoms of the material together (cohesive forces) and influence the formation or reduction of novel surface contacts (adhesive forces). Depending on the forces acting on the liquid it may gain energy by balling up to keep the wetted area small or by spreading and covering a large amount of the solid surface. The behaviour of liquids on surfaces

has gained much attention in recent years, based on the desire to control wetting processes at surfaces to achieve, e.g., self-cleaning, non-icing or low-friction surfaces. Wetting research started with the description of a sessile droplet resting on an ideal surface, which was first described by Thomas Young in his famous equation [1] that connects the surface free energy of the solid γ_{SV} , the surface tension of the liquid γ_{LV} and the interfacial tension between solid and liquid γ_{SL} with the contact angle θ^* of the droplet (see Figure 1):

$$\cos \theta^* = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

The contact angle is defined as the angle enclosed by the tangent of the droplet circular cap shape at the point where liquid, solid and vapour meet. A surface that shows a water contact angle of below 90° is called hydrophilic. A surface, with a contact angle above 90° is called hydrophobic. Superhydrophobic refers to surfaces that show a water contact angle of $> 150^\circ$ and roll off angles of less than 10° [2] [3]. In a classical contact angle measurement, a droplet is placed on the surface and the contact angle is determined by analysing the shape of the droplet. The contact angle observed by such an experiment is referred to as the apparent contact angle.

Influence of surface heterogeneity

Real-life surfaces are rarely homogeneous, and the idealized situation described by Young is not sufficient to describe wetting phenomena at these surfaces. Wetting is largely influenced by the surface structure, i.e. the roughness and chemical composition of the material surface. Among the first to study the influence of surface heterogeneity in terms of chemical inhomogeneity and roughness were Wenzel [4] and Cassie [5]. Wenzel's theory states, that on a rough surface, the apparent contact angle θ is the contact angle predicted by Young's equation θ^* multiplied by a roughness factor r . This factor is the ratio of the area effectively

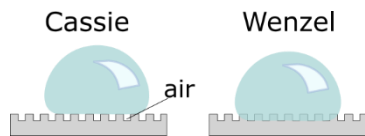


Figure 2: Structural surface heterogeneity, i.e. surface topography influences wetting. In the Cassie-Baxter regime, air is retained between droplet and surface, in the Wenzel state, the drop imbibes the substrate.

wetted by the droplet, considering it wetting all pinnacles and grooves of the surface and the apparent surface area (see Figure 2).

$$\cos \theta^* = r \cos \theta$$

Cassie expanded the Wenzel model by acknowledging that on a sufficiently hydrophobic rough surface, a droplet may rest on the pinnacles of the rough structure thereby not or only partially filling the grooves:

$$\cos \theta^* = f_1 * \cos \theta_1 + f_2 * \cos \theta_2$$

This phenomenon can be observed in nature on the leaves of several plants, for instance on the watermosses *salvinia* which

gave the phenomenon of the droplet resting on the pinnacles with an air layer contained underneath the name “*salvinia* effect”. An important consequence of the Cassie theory is, that when the contact of the droplet with the surface is reduced, the contact angle can be significantly increased. Thus, inducing a tailored roughness in the substrate can increase the contact angle compared to a droplet on the same material without roughness. When analysing a sessile droplet, the following requirements have to be met to guarantee an accurate measurement the droplet is: a) large compared to the chemical inhomogeneity of the surface, b) not too large to eliminate the effects of gravity, c) ideally contained in a closed chamber preventing evaporation.

Influence of surface softness

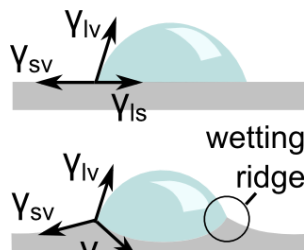


Figure 3: Due to a force acting perpendicular to the surface, a wetting ridge forms on soft materials.

In Young's model the three forces γ_{SG} , γ_{SL} and γ_{LG} act on the resting droplet. The forces parallel to the surface are in equilibrium: γ_{SL} and the horizontal component of γ_{LG} counteract γ_{SG} (see Figure 1). As pointed out early on by Bikerman [6], when the forces parallel to the surface are balanced, there is a resulting force perpendicular to the surface, i.e. the vertical component of $\gamma_{LG} = \sin \theta \gamma_{LV}$, pulling the surface outwards [7, 8]. The deformation of the solid, or “elastocapillary length” is in the order of $d = \gamma_{SG}/E$ [9], where E is the Young's modulus of the material. On hard materials, e.g. materials with Young's moduli in the order of gigapascals, such as metals or glass, these forces lead to a negligible deformation of

the surface in the range of picometers, which surpasses the range of surface roughness usually in the order of nanometers. On soft materials such as elastomers or gels which possess Young's moduli in the range of kilopascals, the elastocapillary length becomes relevant, leading to a wetting ridge that can be microscopically observed (see Figure 3). Wetting ridges have been studied extensively in terms of form and appearance. Experimentally it was found that at an elastic modulus of less than 5 MPa the wetting ridge becomes macroscopically observable [10]. Such softness gradients can also induce droplet movement (durotaxis) towards the softer area on materials [11].

Dynamic Wetting on static substrates

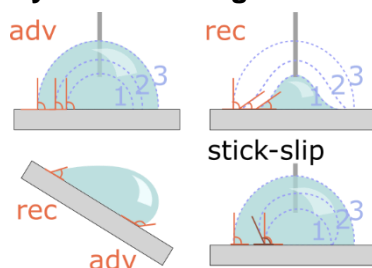


Figure 4: Dynamic wetting is characterized by the wetting hysteresis, the difference in observable contact angles (advancing, adv and receding, rec) and the stick-slip motion.

Under real-world conditions, the wetting of a surface is a dynamic process: When a droplet is placed on a surface, the contact area between surface and droplet changes (increases) before the equilibrium is reached as the system aims toward minimizing the total free energy. To elucidate the dynamics of a liquid wetting a surface, two basic experiments have been proposed: a) the increase in drop volume by injecting fluid into the resting droplet, which will increase the contact area between droplet and surface and the consecutive reduction of the drop volume which will reduce the contact area again, and b) the tilting of a substrate with a resting droplet, causing the droplet shape to deform and at a certain point causes the sliding of the droplet off the surface (see Figure 4). In both cases, the apparent contact angle changes significantly: upon

expanding the droplet, the contact angle increases until it reaches a critical value and the contact line begins to move forward (advancing contact angle) or recedes upon reduction (or evaporation) of the droplet volume (receding contact angle). In case of the tilted surface, the two contact angles become apparent in the droplet shape with a high contact angle (advancing) in front of the droplet and a lower contact angle at the end of the droplet (receding) as shown in Figure 4. Thus, in dynamic wetting several different contact angles can be observed in between the maximum (advancing) and minimum (receding) contact angle. This difference in measurable contact angles is characteristic for the dynamic wetting process and is referred to as the contact angle hysteresis [12]. The apparent contact angle predicted by Young's equation lies between the maximum and minimum value and represents one of the energetic minima available. There are two different types of hysteresis: one associated with different contact angles of resting droplets on the same substrate (static hysteresis) and one associated with a moving contact line of a finite velocity (dynamic hysteresis) [12, 13, 14]. The hysteresis influences the droplet motion on substrates: When a droplet slides down a heterogeneous surface or the droplet volume increases or decreases, the contact angle often does not change smoothly, but rather remains unchanged and then changes suddenly and drastically. This transition between pinning and sliding is referred to as the "stick-slip motion" and occurs on topologically and chemically inhomogeneous surfaces [15, 16]. The motion originates from the tail of the droplet depinning while the front of the droplet jumps over the heterogeneities. Even nanoscale imperfections can be sufficient to induce hysteresis phenomena [17] if the droplets are small enough to "sense" the surface defects. Thus droplet motion can be influenced by surface heterogeneity: It has been shown that droplets placed on hydrophilic/hydrophobic strip patterns slide more easily parallel to the stripe pattern than perpendicular to it [18, 19]. Depending on the surface structure, droplets may pin instead of rolling off, even if the chemistry of the surface is rather hydrophobic as illustrated by the *rose petal effect* compared to the *lotus effect* [20]. Laplace pressure also plays an important role since sliding droplets suffer from a pressure difference due to the difference in droplet curvature, the resulting force counteracts gravity and keeps the droplet sticking to the inclined surface [21, 22].

The significance of the three-phase contact line (3PCL)

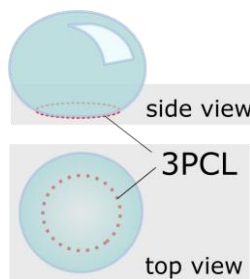


Figure 6: The 3PCL, where gaseous phase, solid and liquid phase meet.

Dynamic wetting conditions describe the case of a moving liquid, e.g. considering a spreading droplet or a sliding droplet. In this case, the three-phase contact line (3PCL), the line "under" the droplet where liquid, solid and gaseous phase are in contact (see Figure 6), plays an important role. It was found that the apparent contact angle is dependent only on the chemical [23] or structural heterogeneity [24, 25] under the 3PCL. Thus, when an inhomogeneity on the surface is completely covered by a droplet, i.e. the 3PCL is not in contact with the heterogeneity, the apparent contact angle appears to be that of the homogeneous surface surrounding the heterogeneity. This "failure" [25] of the classical laws of Young, Cassie and Wenzel can be explained by the foundation of the theories that are based on minimization of the energy change and not on absolute energy changes in a wetting situation [26].

It is now widely accepted that only large droplets that are large compared to the chemical inhomogeneity of a surface follow CB or Wenzel laws. The local conditions at the 3PCL determine the actual visible CA, the surface contact area determines the most stable actual CA [27]. The forces acting at the 3PCL are significant and can even lead to the breaking of rigid nanostructures [28]. Such deformation of the surface lead to a change in

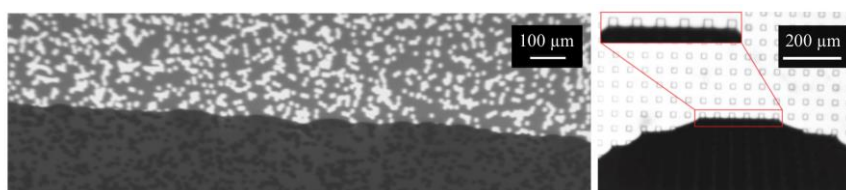


Figure 5: Experimental observation of the 3PCL by microscopy. The 3PCL is not circular but deforms when the system tries to minimize its free energy [29, 30].

properties and may also cause the droplet to stick to the surface. The shape of the 3PCL can be analysed experimentally and it is found that the minimization of energy leads to a “deformation” of the ideally circular shaped line, which can be observed by microscope (see Figure 5Figure 3) [29, 30]. Early studies on the 3PCL were conducted in capillaries with different surface properties [31], and thin fluidic film protruding from droplets can be visualized by fluorescence [32]. The intricate droplet motions especially the dynamics at the 3PCL are still not fully understood. In hydrodynamics the “no-slip” boundary condition for a fluid passing a solid, demands that there is a layer of fluid attached to the solid at all times: the moving fluid comes into contact only with this stationary layer of fluid. A moving contact line however is a clear violation of this concept and the shear stress approaches infinity when approaching the interface between solid and moving liquid [33]. Theoretical approaches therefore either include the contact line dynamics by introducing a slip boundary condition, or by introducing energy dissipation principles.

Dynamic wetting on dynamic substrates

Recently, much effort has been put into understanding the dynamic wetting on substrates with dynamic wetting properties because they represent a more accurate picture of naturally occurring wetting phenomena. Understanding the influence of dynamic surfaces, i.e. flexible, adaptive and/or switchable surfaces on wetting behaviour could lead to a new generation of robust smart surfaces that could one day solve many everyday challenges and contribute to saving energy and water resources.

Dynamic wetting on soft substrates plays a major role in nature, since biological systems such as cells and tissues are soft compared to technical substrates. It is suggested that cells may sense the stiffness of their environment and thus react to tissue surface tensions, a process that is important for tissue spreading [34, 35]. As shown above, when a droplet is placed on the soft surface, a wetting ridge forms (see Figure 3). When the 3PCL moves across the surface, the wetting ridge moves with it [36] so that the droplet movement is largely influenced by the viscoelastic properties of the substrate because it has to be constantly deformed in the process. Thus processes like spreading are considerably slowed down on soft substrates [37] and energy can dissipate via the viscoelasticity of the solid [38]. The deformation thus causes a droplet retention force that prevents droplets from sliding, with bigger droplets sliding more easily due to the influence of gravity [39, 40]. Gels possess complicated wetting properties, since the wetting liquid may also enter the substrate and change its wetting dynamics, and molecules become more mobile in the gel structure and may change their orientation dynamically. Early studies determined that the contact angle of water on a water-soluble material was not, as expected, 0° , but had a finite value, i.e. surfaces appeared to be partially hydrophobic even though the material is hydrophilic [41]. It was found that the contact angle is a function of the water content of the polymer, a behaviour that is attributed to a reorientation of polymeric chains in gels to expose more hydrophilic or hydrophobic components at the surface, depending on the relative humidity, e.g. the surrounding vapour phase [41, 42, 43, 44]. Hydrogels may also exert reversible switching behaviour due to shape-memory effects [45] or swelling behaviour [46]. Hydrogels may be produced with different elastic moduli dependent on the amount of crosslinking in the gel. Therefore, hydrogels represent an excellent material for the study of dynamic processes as proposed by this SPP because they unite properties of adaptability, flexibility and switchability. A particularly interesting class of gels are photorheological gels that switch their viscosity in response to light. Different viscosities or elastic moduli lead to the phenomenon of durotaxis, where droplets move towards areas of lower elasticity [11]. This mechanism could be an interesting method for inducing droplet movement on dynamic substrates.

Dynamic wetting on switchable substrates: Surface-bound or material-integrated molecular switches are capable of changing the surface energy of substrates. Photoswitches are especially interesting, because the switch can be spatially controlled by the controlled exposure to light. Spiroyrans (SP, see Figure 7) are an especially interesting class of molecular switches because the closed ring spiroyrans- and the open-ring merocyanine (MC) forms are vastly different [47]. The switch between hydrophobic SP (colourless) and hydrophilic MC (magenta) has been reported in bulk and in monolayers.[48, 49] On smooth

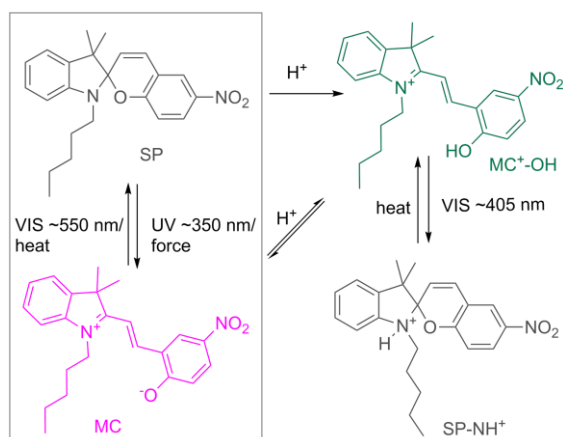


Figure 7: Switching dynamics of spiropyrans on surfaces.

of the surface, e.g. by laser light. This way, LIPSS (laser induced periodic surface structures) can be created that have been shown to influence surface wetting [54]. Thus, the combination of rough surfaces with SP switches is expected to lead to a large difference between the switched and unswitched state. Switching of SP-containing polymers can be induced by light as well as by mechanical stress [55, 56]. The switch between SP and MC can be achieved by UV light, and is reversible under visible light or heating. The switch can also be induced under acidic conditions, giving rise to different types of protonated species like MC^+-OH and $SP-NH^+$ [57] [58] (see Figure 7). The only coloured species in the scheme are MC (purple) and MC^+-OH (green). Interestingly, under acidic conditions reverse photochromism [58] is observed, where open-ring form green MC^+-OH can be converted to close-ring colourless $SP-NH^+$, a conversion that is also accompanied by a large change in dipole moment due to the switch between SP and MC form. Bifunctional SP have been developed that also switch under the influence of force (mechanoswitching, see Figure 8). Fluorinated environments are known to elevate the efficiency of the photochromism, therefore copolymers with fluorinated compounds could be an excellent option for generating surfaces with high switching efficiency [59]. Mechanoswitching can also be induced by magnetic force. The introduction of magnetic nanoparticles is an efficient way to achieve spatially controlled magnetic activation. Magnetic nanoparticles have been used to switch the wetting properties of surfaces in various ways. Functionalized magnetic particles can be

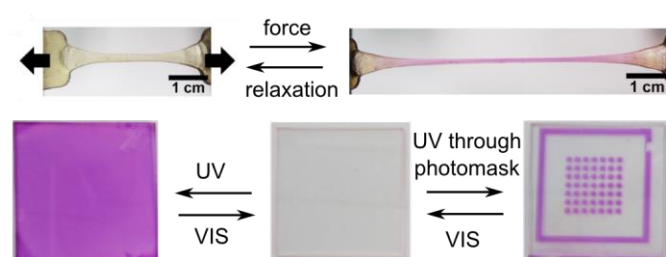


Figure 8: Mechanoswitching of bulk spiropyran materials reported by Gosweiler *et al.* [63] and photoswitching of surface-bound spiropyran materials reported by Schenderlein *et al.* [48].

attracted to the surface by magnetic force and thus change the wetting properties of, e.g. electrodes [60]. Magnetic particles in thermoresponsive polymers have also been used for hydrophilic/hydrophobic phase separation [61] and for the deformation of superhydrophobic post-structures, to induce the switching of wetting states [62]. It has been shown that spiropyran can be switched by mechanic forces [63]. Thus, the introduction of magnetic particles in

materials with spiropyran functionalities are expected to lead to magnetoswitchable materials, that can be used to study 3PCL dynamics on switchable materials.

Preliminary work and expertise

In our chemistry and materials science-based research group we have acquired detailed knowledge about the synthesis of porous polymers in terms of compounding and processing. We have previously shown the fabrication of tailored micro-/nanostructured porous polymers with superhydrophobic wetting properties [64]. Depending on the porogens (non-solvents) in

the compounding mixture, the porosity and structure of the material can be adjusted. This “roughening” of the structure by introducing porosity leads, as predicted by Cassie (see Figure 2), to enhanced superhydrophobic properties. Such rough surfaces pose ideal substrates for the immobilization of co-polymerization of spiropyran (SP) moieties, because the rough structures will further enhance the switch in contact angle on SP-functionalized surfaces. The micro-/nanostructured polymer foam “Fluoropor” possesses a low Vickers hardness of 1.19 HV (100 mN/20s) and is extremely flexible (see Figure 9) – lending itself well to mechanoswitching experiments with spiropyrans. Besides polymer structuring our group has ample experience in the field of surface functionalization. We have demonstrated a reliable method for the fabrication of surface patterns “BioBitmaps” via photoimmobilization of fluorescently-labelled molecules on various substrates such as glass [65, 66] or paper [67] as well as on the porous Fluoropor substrates (Figure 9). The custom-developed BioBitmaps technology is a universal tool for surface functionalization and for generating surfaces for the study of wetting behaviour. The combination of micro-/nanostructured polymer foam with the functionalization using the BioBitmaps technology will enable the formation of switchable surfaces that allow large changes in surface energy upon switching and thus large changes in contact angle. To achieve BioBitmaps surface functionalization with high lateral precision our group has previously reported a custom-developed photolithography system based on a digital mirror device (DMD) for maskless photolithography that can be used to expose surfaces to intricate, greyscale patterns of light of tuneable wavelength. This system is a useful tool in studying the dynamics of droplets upon photoswitching of surfaces, because it will enable the switching underneath the droplets with high spatial precision in order to study the droplet behaviour in response to this dynamic. Our group has also previously studied surface switching by electric energy (electrowetting, see Figure 9) on polymer foams and the switching of azobenzene surfaces and is equipped with all relevant equipment for studying classical wetting processes.

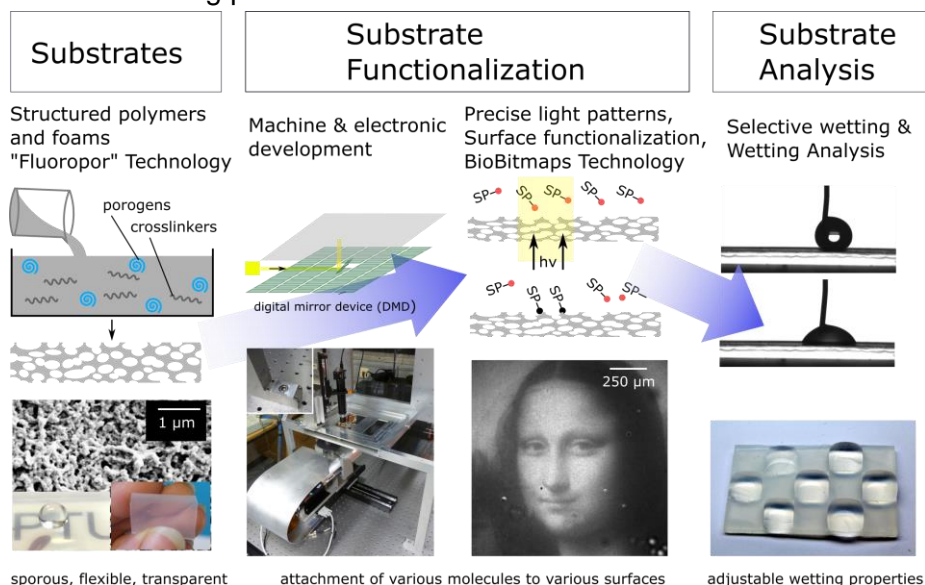


Figure 9: Expertise of the applicant relevant for this proposal: The formation of porous polymer substrates with special wetting properties, e.g. transparent micro-/nanostructured polymer foam Fluoropor, which is flexible and shows high water repellency. Substrate functionalization by DMD-based maskless lithography for the immobilization of molecules on surfaces by photo-bleaching. Substrate Analysis: Electrowetting and analysis of adjustable wetting properties.

Integration into the Schwerpunktprogramm (SPP)

The aim of this project is to monitor the dynamic behaviour of the 3PCL of droplets on dynamic substrates such as switchable spiropyran surfaces and gels. This project will make a significant contribution to the fundamental understanding of contact line dynamics by studying real-world surfaces, i.e. surfaces generated outside the clean room in a standard laboratory environment, which are generally heterogeneous and give rise to phenomena like contact angle hysteresis, droplet pinning and stick-slip motion. The movement of the contact lines will be studied by experiment, e.g. by high-speed camera and the influence of the substrate on the macroscopic dynamics will be studied in real time. This project will provide answers to the question if changing substrate properties underneath a wetting film or droplet

can induce droplet motions or dewetting phenomena. The following collaborations are planned for this proposal and further described in 2.8:

- Magnetic actuation of Spiropyran switch – Collaboration with E. Gurevich (Bochum)
- Theoretical evaluation of 3PCL movement – Collaboration with D. Peschka (Berlin)
- Structuring of polymer surfaces – collaboration with F. Müller (Jena)

Application for traveling funds

This project will strongly benefit from the exchange between research groups in the SPP. Workshops and schools organized within the SPP will help to evaluate and discuss data. To ensure visibility of the SPP and the research group, the most relevant international conferences will be attended. Within this project we would like to strengthen the cooperation between theoretical and experimental groups by welcoming theoreticians to our institution and further the understanding of theoretical models for experimentalists. This project therefore includes application for travel funds.

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

- Micro-/nanostructured Polymers with special wetting properties: D. Helmer, N. Keller, F. Kotz, F. Stolz, C. Greiner, T. M. Nargang, K. Sachsenheimer, B. E. Rapp: „Transparent, abrasion-insensitive superhydrophobic coatings for real-world applications”, *Nature Scientific Reports*, 7, 1, 15078, 2017.
- BioBitmaps for the functionalization of surfaces: T. M. Nargang, M. Runck, D. Helmer, B. E. Rapp: "Functionalization of paper using photobleaching: a fast and convenient method for creating paper-based assays with colorimetric and fluorescent readout", *Engineering in Life Sciences*, 16, 525-531, 2016.
- DMD-based photolithography system: (a) A. Waldbaur, B. Waterkotte, K. Schmitz, B. E. Rapp: "Maskless projection lithography for the fast and flexible generation of grayscale protein patterns", *Small*, 8, 10, 1570-1578, 2012. (b) F. Kotz, K. Arnold, W. Bauer, D. Schild, N. Keller, K. Sachsenheimer, T. M. Nargang, C. Richter, D. Helmer, B. E. Rapp: "Three-dimensional Printing of Transparent Fused Silica Glass", *Nature*, 544, 337-339, 2017.

1.1.2. Other publications [not applicable]

1.1.3. Patents

1.1.3.1. Pending

- B. E. Rapp, D. Helmer, C. Richter, N. Keller: "Hochfluorierte nanostrukturierte Polymerschäume zur Herstellung superabweisender Oberflächen", DE102016012001A1, 2016.
- B. E. Rapp, D. Helmer, C. Richter, N. Keller: "Highly fluorinated nanostructured polymer foams for producing super-repellent surface", WO2018065094A1, 2016.

1.1.3.2. Issued [not applicable]

2. Objectives and work programme

2.1. Anticipated total duration of the project

In accordance to the call the project will run for the first three years of SPP 2171 with a envisioned extension to the full six-year period of the SPP in a the follow-up. The project is planned to start at 01.10.2019.

2.2. Objectives

In this proposal, we will study nano-/microstructured polymer foams functionalized with SP which will be switched reversibly, dynamically and at high resolution for studying the dynamics of the 3PCL of water droplets on the surface before, during and after the switch.

The switch of SP to merocyanine MC is clearly visible by the purple color of the MC form. Upon switching, the surface energy of the material is changed and this change in energy influences the macroscopic behavior of water droplets on the surface of the material. Previously reported structured polymers foams with adjustable porosity [64] serve as the substrates. Functionalization of these substrates with SP will be achieved by our previously reported BioBitmaps technology[65] (surface functionalization) or by the generation of novel porous polymer mixtures containing SP (bulk functionalization). Switching of the SP will be selectively induced by our DMD-based system, or by mechanoswitching through stretching or magnetic activation using nanoparticles. By observing color change and droplet shape from the side and from the top this project aims at understanding the dynamics of water droplets on SP polymers. By observing color change and droplet shape from the side and from the top we will address the following properties of **“switchable” SP surfaces**:

- possibility of switching SP on the surface under a resting water droplet
- resulting macroscopic behavior of the droplet and dynamics of the 3PCL
- droplet dynamics dependent on the percental area switch under the 3PCL
- wetting dynamics on hydrophilic/hydrophobic patterns of different feature sizes

This proposal will also address **“adaptive” SP surfaces** by analyzing the movement of slightly acidic droplets that convert merocyanines to a stable, protonated form of green colour. The following points will be addressed:

- influence of MC protonation on contact angle and water droplet movement dynamics
- movement dynamics and behavior of slightly acidic droplets on SP and MC surfaces.

This proposal will also study droplets on **“flexible” SP surfaces**, i.e. SP-based photorheological gels that change their stiffness upon irradiation:

- dynamics of droplet movement due to a softness gradient (durotaxis)

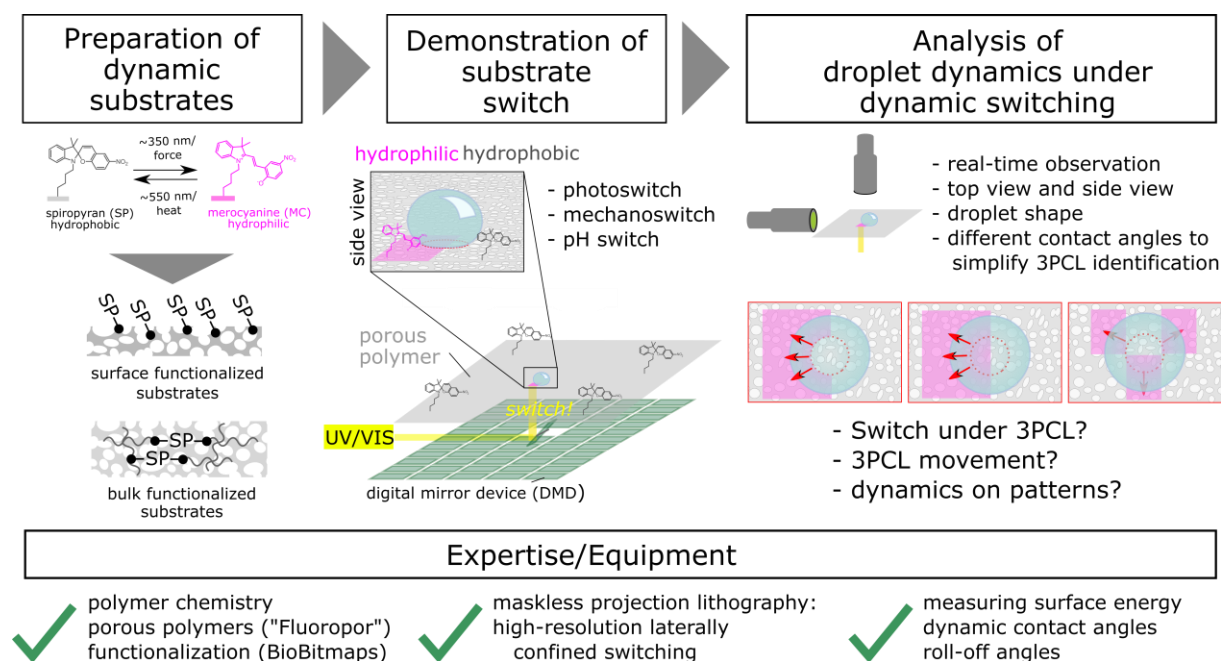


Figure 10 Overview of the fundamental objectives of this project. In the course of this project, polymers with surface functionalization or bulk functionalization based on switchable spiropyrans (SP) will be used. The SP switch induced by light (photoswitch), force (mechanoswitch) or pH causes a change in the surface energy of the materials, e.g. a hydrophobic surface becomes hydrophilic. This effect is enhanced by using porous polymer surfaces to maintain a Cassie-Baxter wetting state. Droplets on the switchable substrates will be monitored by high-speed camera from below and above and droplet dynamics under changing substrate properties will be analyzed. Our group has expertise in all parts of this project: polymer chemistry and the fabrication of porous polymers, the functionalization of the polymers by the BioBitmaps technology, the use of a high-resolution maskless lithography system for spatially confined light exposure and the analysis of dynamic wetting phenomena.

2.3. Work programme incl. proposed research methods

This work is divided into four work packages (WP): WP 1 Synthesis of functional SP, WP 2 Dynamic SP substrates, WP 3 Evaluation of properties and switching of functional SP polymers, WP 4 Droplet dynamics on SP polymers.

WP 1 Synthesis of functional SP: WP 1 will focus on the synthesis of SP molecules with functional groups that allow for the inclusion of SP into polymeric materials as a surface functionalization and as a bulk functionalization. The work package is divided into WP 1-1: “Monofunctional SP”, WP 1-2 “Bifunctional SP”, WP 1-3 “Analysis of SP photoswitch in solution”. Monofunctional and bifunctional SP molecules will be synthesized containing methacrylate, acrylate or amino groups. See Figure 11 for an overview of the synthesis strategies explored in WP 1. **WP 1-1 “Monofunctional SP”** will provide switchable monofunctional SP molecules. The synthesis of monofunctional SP molecules has been previously reported.[68],[48] 2,2,2-Trimethylindolenine is reacted with an alkyl iodide to introduce a functional group for further reaction and consecutively reacted with 5-nitrosalicylaldehyde to give the final SP. **WP 1-2 “Bifunctional SP”** provides bifunctional SP for the integration as crosslinkers in bulk polymers. The synthesis of bifunctional SP can be achieved according to the protocol of Gossweiler [63]. Here, a second alcoholic group is introduced by reaction with 2,3-dihydroxy-5-nitrobenzaldehyde. Monofunctional carboxyl-group and bifunctional alcohol groups can be used to introduce further desired functional groups such as methacrylates or amines via esterification or carbodiimide coupling of amines [48, 63]. **WP 1-3 “Analysis of SP photoswitch in solution”** will ensure the functionality of the synthesized SP by analysis of the photoswitching behaviour in solution. For this purpose, SP are diluted in different solvents and exposed to UV light. The time for the photoswitch reaction and the UV/VIS spectra of the compounds will be recorded.

In summary, WP 1 will provide at least one switchable SP molecule for the immobilization on surfaces and/or the incorporation into a bulk polymer. SP synthesis has been previously reported by different sources and is expected to pose no difficulty especially considering the organic chemistry background of the applicant. The synthesis of the molecules is therefore not expected to require more than six months, with an additional total of three month for studying and confirming the switchability and properties of the switching process in solution (see Figure 16).

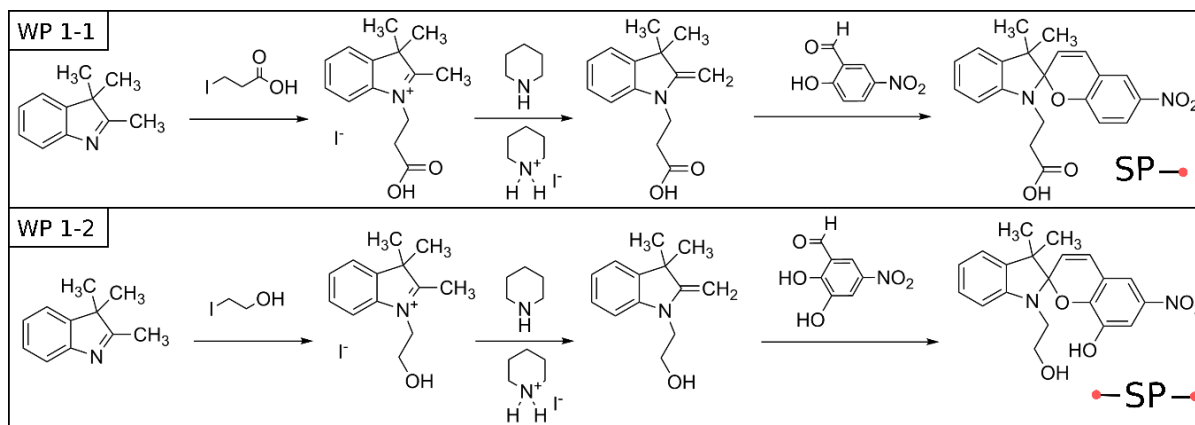


Figure 11: Synthesis strategies for WP 1, providing mono- and bifunctional spiropyrans (SP). The synthesis of spiropyran derivatives for surface functionalization (monofunctional carboxylic acid) and bi-functional alcohol for bulk functionalization of polymers is well studied and can be executed according to Schenderlein and Gossweiler [48, 63].

WP 2 Dynamic SP substrates focusses on introducing the switchable SP molecules provided in WP 1 into functional polymeric substrates. WP 2 provides several options for achieving this goal based on the choice between mono- and bifunctional SP monomers from WP 1 and the choice between SP introduction into the bulk or the surface of functional polymers for photoswitching or mechanoswitching (stretching). In a further approach, photorheological SP based gels will be generated to analyse the durotaxis of droplets on dynamic substrates. WP 2 is divided into WP 2-1 “Photoswitchable smooth SP polymers”, WP 2-2 “Photoswitchable porous SP polymers”, WP 2-3 “Mechanoswitchable SP polymers”,

WP 2-4: “Photorheological SP gels”, WP 2-5 “LIPSS wetting enhancement”. See Figure 12 for an overview of WP 2. **WP 2-1 “Photoswitchable smooth SP polymers”** will provide photoswitchable smooth SP polymers by (1) introducing SP groups to the surface polymers by the BioBitmaps technology and (2) introducing SP groups into the material by copolymerization of SP acrylates. For the copolymerization different acrylates will be tested: hydrophobic fluorinated acrylates based on the Fluoropor technology as well as standard hydrophilic acrylates such as 2-hydroxyethylmethacrylate (HEMA). **WP 2-2 “Photoswitchable porous SP polymers”** will provide the corresponding porous SP polymers, by (3) introducing SP to the surface of rough polymers (generated by the Fluoropor technology) with the BioBitmaps technology and by (4) copolymerization of SP acrylates with porogens and hydrophilic or hydrophobic acrylates.

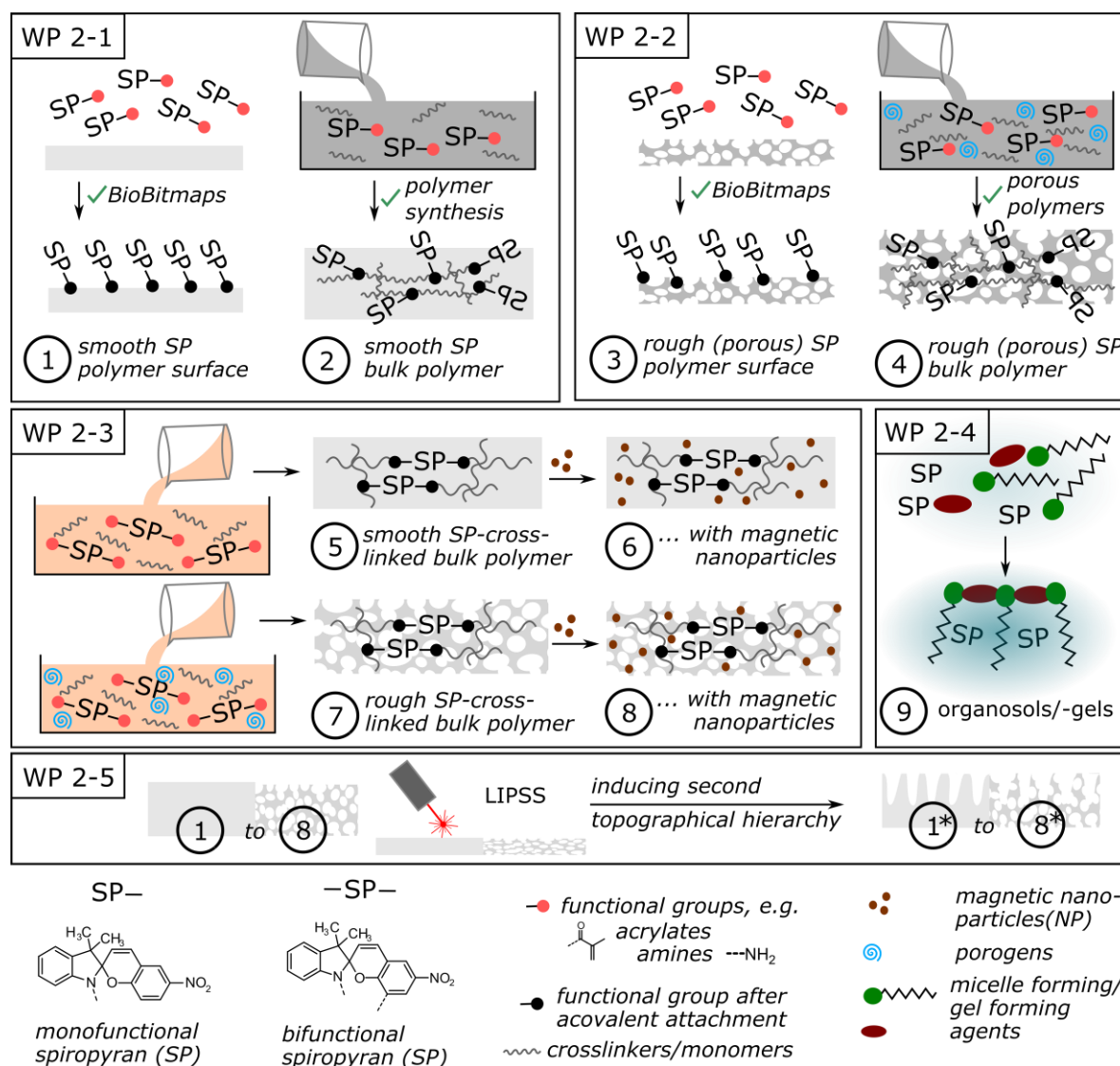


Figure 12: Overview of WP 2. WP 2-1 provides photoswitchable smooth polymers based on monofunctional SP. Here, SP functionalization will be introduced by (1) surface-functionalization via the BioBitmaps technology and by (2) copolymerization of monofunctional SP acrylates with hydrophilic- or hydrophobic acrylates. WP 2-2 provides porous polymers with monofunctional SP (3) on the surface (immobilized by the BioBitmaps technology), and (4) in the bulk (produced by copolymerization). WP 2-3 provides mechanoswitchable SP polymers based on bifunctional SP crosslinkers to give (5) smooth or (7) porous SP polymers. Mechanoswitching of the polymers will be induced by magnetic nanoparticles (NP) in the polymer mixture, included in substrate types (6) and (8). Nanoparticles are fabricated in collaboration with Evgeny Gurevich and Jeanette Hussong (University of Bochum). WP 2-4 attempts to produce photorheological SP gels from commercially available components.

The applicant has substantial knowledge in generating porogen/monomer mixtures for the generation of porous polymers. The functionalization of polymer substrates including porous polymers has been previously shown (see Figure 9) and thus substrates (1) and (3) are

readily available and are expected to require no more than three months fabrication time. For substrate types (2) and (4) the highly hydrophobic Fluoropor mixtures likely have to be adjusted by adding emulating agents to accommodate the attachment of SP, for these substrates a fabrication period of seven months is expected. In **WP 2-3 “Mechanoswitchable SP polymers”** the bifunctional SP from WP 1-2 will be used to produce (5) smooth and (7) porous SP polymers. In addition, magnetic nanoparticles (NP) will be added to these mixtures to produce magnetically switchable (6) smooth and (8) porous SP polymers. Magneto-switchable SP polymers (6) and (8) will be produced and evaluated in cooperation with E. Gurevich (University of Bochum, see 2.8 for details). In this part, Fluoropor polymer mixtures also have to be optimized to accommodate SP in the mixture. For optimization a period of seven months' time is estimated. **WP 2-4 “Photorheological SP gels”** will evaluate a simple method reported by Lee[69] to produce photorheological SP based gels by mixing sodium lecithin, sodium deoxycholate and a commercially available, N-methylated SP. The gels are produced in cyclohexane and are thus expected not to mix with water droplets enabling the study of droplets on the gel surface. Cyclohexane is a fast evaporating liquid and may have to be exchanged for a less volatile compound and efforts will be made to optimize the gel mixture reported by Lee with an estimated time requirement of five month. If this strategy fails at producing the desired effects, droplets will be analysed in well-closed chambers. **WP 2-5 “LIPSS wetting enhancement”** aims at inducing a second structure hierarchy in porous and smooth substrates by laser induced periodic structuring. Different secondary topographic structures will be introduced by laser induced periodic surface structuring (LIPSS) in cooperation with Frank Müller (University of Jena) [54]. Another micrometre-sized structuring could significantly enhance the hydrophobicity of the SP substrates. This aims at enhancing the difference between achievable contact angles before and after the switch. LIPSS will be introduced into the polymer surface in two ways: either by directly exposing the polymer to the laser, which will cause a small-scale LIPSS (millimetres), or by employing a replica casting process, which will result in a larger scale (several centimetres) LIPSS. This is estimated to require three months.

In summary, WP 2 provides dynamic SP substrates based on the generation of porous polymers by the Fluoropor technology and the immobilization of SP molecules by the BioBitmaps technology. The Fluoropor technology will be expanded to accommodate the fabrication of hydrophilic porous polymers and to accommodate the introduction of SP molecules and magnetic nanoparticles into the polymer mixture. In addition, a photorheological SP gel will be produced as previously shown in the literature, completely based on commercially available compounds. WP 3 will provide at least one dynamically switchable SP based surface.

WP 3 Evaluation of properties and switching of functional SP polymers focusses on

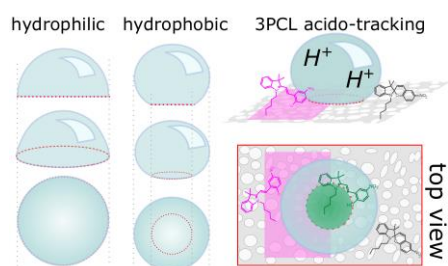


Figure 13: “Acido-tracking” of 3PCL. The 3PCL under hydrophilic droplets is readily visible. 3PCL of hydrophobic droplets is smaller than the lateral droplet size which complicates detection. Acido-tracking of the 3PCL due to colour change in the droplet/substrate contact areas due to MC protonation could simplify 3PCL detection.

testing the dynamic surfaces generated in WP 2 for their dynamic switching properties. All surfaces generated in WP 2 will be evaluated in terms of contact angles, roll off angles, visibility (colour change) of the switch, temporal stability of the switch, pattern generation and lateral size limitations of the switch. WP 3 is divided into 3 work packages: WP 3-1 “Properties of switchable substrates”, WP 3-2 “Properties of adaptive substrates” WP 3-3 “Properties of flexible substrates” (see Figure 14).

WP 3-1 “Properties of switchable substrates” focusses on analysing the properties of switchable substrates (1) to (8) before and after switching in terms of surface energy, contact angle, roll-off angle (advancing and receding angles). It will be evaluated if monolayer colour change is directly visible. If monolayers are not visible, the illumination spot projected onto a monolayer substrate can be used to identify areas of switch/no switch. Switching by stretching of substrates (5)-(8) and switching

by magnetic force on substrates (6) and (8) will be evaluated. The inherent flexibility of Fluoropor foams (see Figure 9) suggests that switching is possible upon bending or stretching of the foam. It will be tested if magnetoswitching via magnetic nanoparticles can lead to spatially confined areas of switching by local introduction of magnetic force. **WP 3-2 “Properties of adaptive substrates”** will determine the adaptive properties of SP substrates (1) to (8) by inducing a switch from SP to MC and determining the influence of slightly acidic droplets upon contact angles (advancing, receding, roll-off angles). We will elucidate if the switch from MC (purple) to MC-OH⁺ is visible (green colour) and if it significantly influences substrate properties such as surface energy. We will evaluate if this method can be used for “acido-tracking” of the 3PCL, because the slightly acidic character of the droplet will induce a colour change only in the regions of the droplet in contact with the substrate. In this way, the 3PCL could be identified under a hydrophobic droplet (Figure 13). We will assess if the colour change can be used for tracking under these conditions. **WP 3-3 “Properties of flexible substrates”** evaluates the viscosity switch in SP-based photorheological gels and determines surface energy and contact angles of the substrates. The gels change their viscosity in the range from 1,5 Pa s to 0,1 Pa s [69] and are thus soft enough to produce a wetting ridge. The ridge will be visualized by camera and analysed before and after switching.

In summary, WP 3 provides insight on the dynamic properties of the substrates and aims to characterize these properties to present an accurate description of the macroscopic behaviour of substrate dynamics.

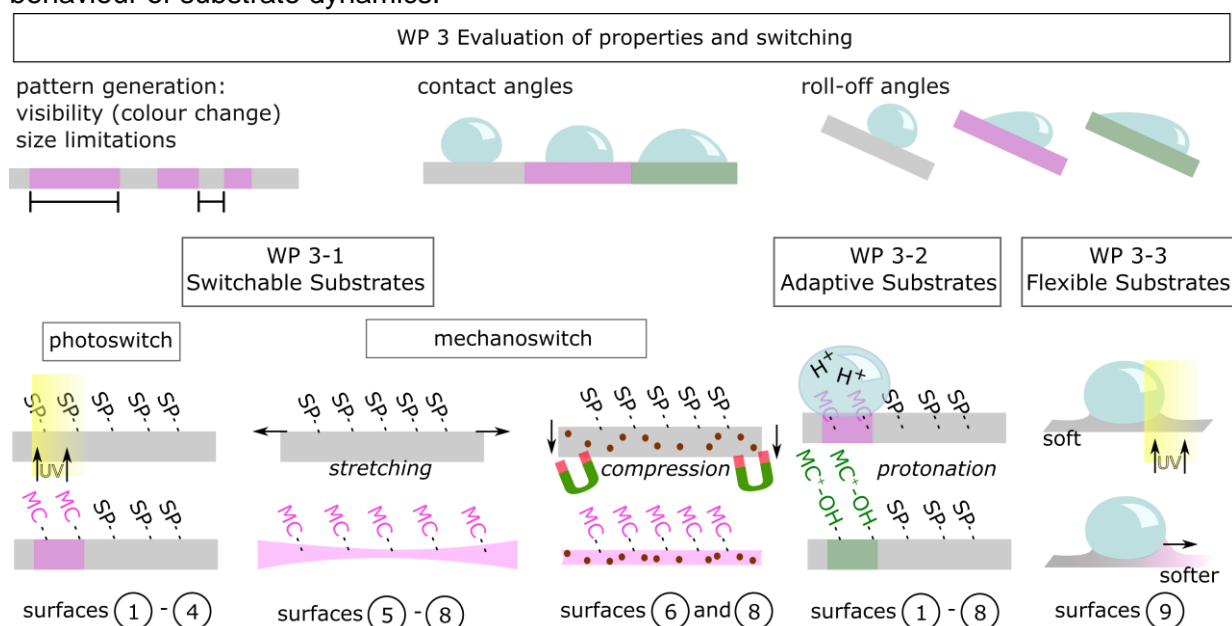


Figure 14: Overview of WP 3 which evaluates switching and the resulting properties of substrates generated in WP 2. The switchable, adaptive and flexible substrates generated in WP 2 will be evaluated in terms of their individual dynamics. Surfaces (1)-(4) will be photoswitched, substrates (5)-(8) will be mechanoswitched, substrates (1)-(8) will be tested for adaptive switching of the MC state to the MC-OH⁺ state. Photorheological gels (9) will be tested for viscosity switching. All switching events will be evaluated in terms of pattern visibility (colour change), pattern size limitations, apparent contact angles and roll-off angles, advancing and receding contact angles.

WP 4 Droplet dynamics on SP polymers will provide insight into the behaviour of droplets on the surfaces under dynamic switching. For this purpose, a system will be developed for analysing droplet movement from the side and from the top. The switch will be induced by our maskless projection lithography system and it will be evaluated if switching can also be induced by weaker light sources such as LED displays to simplify the experimental setup. The induction of movement on sessile droplets upon substrate switching will be studied as well as the behaviour of sliding droplets under switching (barriers). On porous surfaces, the spreading of water containing fluorescent dye on and into the material will be evaluated. In cooperation with D. Peschka (Weierstrass Institute, Berlin) a theoretical description of the

droplet behaviour will be investigated. WP 4 is divided into six work packages: WP 4-1 “Development of highspeed imaging platform, switching based on maskless lithography”, WP 4-2 “Development of highspeed imaging platform, switching based on LED displays”, WP 4-3 “Sessile droplet behaviour during dynamic switching underneath 3PCL”, WP 4-4 “Sliding droplet behaviour under dynamic switching”, WP 4-5 “Evaluation of droplet spreading on porous surfaces”, WP 4-6 “Theoretical evaluation of droplet movement and droplet spreading”, WP 4-7 “Electrokinetically driven surface deformations”. See Figure 15 for an overview of WP 4.

WP 4-1 “Development of highspeed imaging platform, switching based on maskless lithography” will develop a system for tracking the 3PCL. The maskless lithography system will be equipped with highspeed cameras to track the droplet movement. For this purpose, an existing monochromatic camera will be installed parallel to the surface to record the side view of the droplet. A high-speed color camera (e.g. Baumer LXC-20C or VCXU-02C) with colour recording, to enable (see figure Figure 13) will be added above the substrate surface to visualize the droplet and the visible pattern expected during acido-tracking. Alternatively, in **WP 4-2 “Development of highspeed imaging platform, switching based on LED displays”** will develop a system for tracking the 3PCL based on a contact angle instrument available at the host institution, where switching is induced by LED light. It has been previously reported, that SP can be switched by UV LED [70], thus possibly simplifying the experimental setup of the switching experiment. For this purpose, LED displays will be evaluated for switching and a system for droplet tracking with one monochromatic camera parallel to the surface and one colour camera perpendicular to it will be installed. With one or both systems operational, the droplet dynamics on SP substrates will be analysed. **WP 4-3 “Sessile droplet behaviour during dynamic switching underneath 3PCL”** aims at observing a sessile droplet on the dynamic surfaces provided by WP 2 and characterized in WP 3 during surface switching. The colour camera installed above the setup will record any surface switching induced by the switch with the maskless lithography system or the LED display. The droplet movement will be recorded with at least 450 frames per second to detect the reaction of the droplet to the switching under the 3PCL. The experiments will be conducted with all photoswitchable surfaces: (1)-(4) and (9). Droplet velocity and droplet shape will be determined. Mechanoswitchable surfaces will be actuated by stretching (5) and (7) or by magnetic actuation (6), (8). Changes in the droplet shape upon stretching will be compared to SP-containing surfaces that do not switch upon stretching to determine the influence of the surface switch on the droplet shape. **WP 4-4 “Sliding droplet behaviour under dynamic switching”** will study the behaviour of sliding droplets, e.g. on inclined surfaces, using the imaging platform developed in WP 4-1/WP 4-2. Mechanoswitchable substrates (5)-(8) will be switched by stretching and the expected slowing of the droplet will be analysed by imaging. Photoswitchable substrates (1)-(4) will be used to create pattern barriers for droplets, and the droplet behaviour, e.g. droplet shape upon crossing the barrier will be evaluated. **WP 4-5 “Evaluation of droplet spreading on porous surfaces”**: Depending on the pore size of the produced polymers, droplets may imbibe the material upon switching from hydrophobic to hydrophilic SP states. The spreading of water droplets with fluorescent markers will be tracked by fluorescence microscopy in 2D and by confocal microscopy in 3D. **WP 4-6 “Theoretical evaluation of droplet movement and droplet spreading”**: In cooperation with D. Peschka (Weierstrass Institute, Berlin) an attempt will be made to describe the data on droplet behaviour on barriers and droplet behaviour during spreading in a theoretical model (see 2.8 for details). **WP 4-7 “Electrokinetically driven surface deformations”** will provide switchable SP surfaces for measurements of EDSD in cooperation with M. Bercovici (Haifa, see 5.4.1. for details). The pressure of a liquid can be used to exert a force on a soft (elastic) surface to generate reversibly changeable surface deformations [71]. Applying an electric field in a channel with changing surface charge can lead to internally generated pressures that can deform the channel [72]. Using the change in surface energy associated with the SP/MC switch such deformations could be controlled and used to generate surface topographies (bumps, pinnacles) in real time. This will be used to attempt to switch a surface between Cassie and Wenzel states. The droplet behaviour on these topographically changing surfaces will be analysed.

In summary, WP 4 provides a novel analysis platform for droplet observation and utilizes this platform to understand the behaviour of droplets on dynamic substrates.

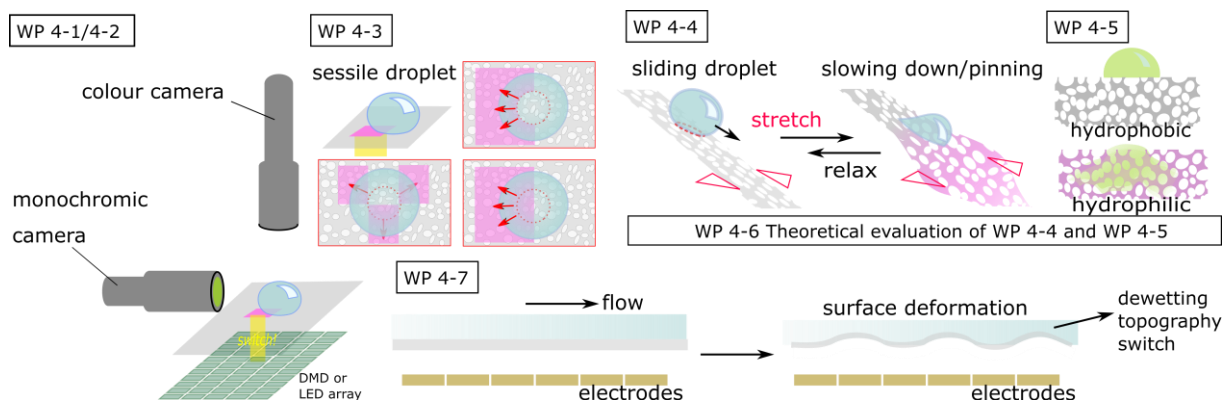


Figure 15 Overview of WP 4. WP 4 aims at developing a high-speed imaging platform by combining the maskless projection lithography system with the setup of a contact angle high-speed camera and an additional perpendicular camera to study droplet shape from above. WP 4-3 will study the behaviour of sessile droplets on dynamic surfaces upon switching. WP 4-4 will study the behaviour of sliding droplets upon switching. WP 4-5 will study the behaviour of droplets imbining a porous surface upon switching. In all experiments, acido-tracking of the 3PCL will be evaluated to visualize “hidden” 3PCL (see also Figure 13). WP 4-6 (collaboration with Dr. D. Peschka, Weierstrass Institute Berlin) aims at providing a theoretical basis of the 3PCL behaviour of droplets sliding over barriers/switched areas and droplet spreading inside porous materials. WP 4-7 (collaboration with Ass. Prof. Moran Bercovici, Technion, Haifa) will study the electrokinetically driven deformation of thin elastomeric films with different surface charges, which will be achieved by SP modified thin films. The surface topography changes will be evaluated for their use in dynamic switching between rough and smooth surfaces.

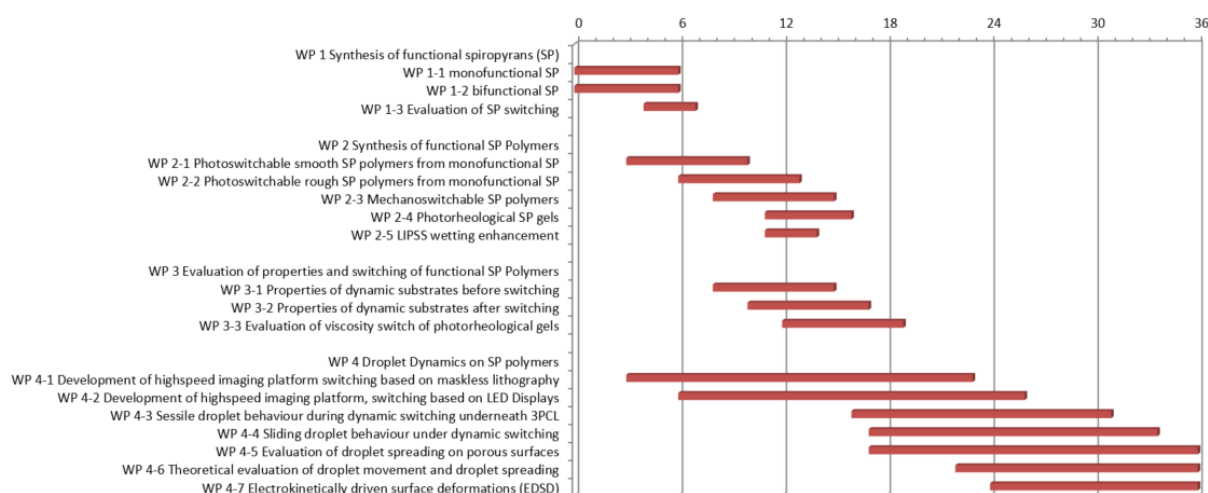


Figure 16 Project plan: Overview of proposed timeline for the project consisting of work packages (WP) 1 to 4.

2.4. Data handling

The acquired research data will be published in peer reviewed journals and presented on international conferences. All data will be long-term archived on a secured back-up protected network server. Any data requested for publication will be made public within the regulations of the publisher. Any further data will be made available to researchers upon reasonable request. Data between collaboration partners will be exchanged via the university's FTP servers to prevent loss or misuse of data.

2.5. Other information [not applicable]

2.6. Description of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern [not applicable]

2.7. Information on scientific and financial involvement of international cooperation partners [not applicable]

2.8. Information on scientific cooperation within SPP 2171

Magnetic actuation of Spiropyran switch – Collaboration with Prof. Evgeny Gurevich and Jun.-Prof. Jeanette Hussong (Ruhr University, Bochum)

Prof. Evgeny Gurevich and Jun.-Prof Hussong (University of Bochum) will provide magnetic nanoparticles produced by laser ablation for the incorporation into spiropyran polymeric materials. The nanoparticles will be introduced into monomeric mixtures containing SP. It will be evaluated if mechanic actuation by an electromagnet will induce bending or compression of the flexible polymer, thus activating the SP switch. The expertise of Prof. Gurevich in the production and handling of the NP in different solvents[73] will be helpful in developing novel monomeric mixtures to provide effective magnetoactive spiropyran polymers.

Theoretical evaluation of 3PCL movement – Collaboration with Dr. Dirk Peschka (Weierstrass Institute, Berlin)

The computational simulation of contact line dynamics can be addressed in different ways, one promising strategy is using a variational approach based on energy dissipation [74]. The model has been previously shown to be in good agreement with experimental results obtained in dewetting dynamics of polymer films [75]. In the collaboration with Dr. Dirk Peschka, a droplet will be observed on a surface with a pattern of different wetting properties, i.e. a barrier will be introduced, that the droplet will have to pass. The droplet deformation upon passing the barrier will be analysed by high-speed camera and compared to the theoretical results obtained. In a second approach, water will be fluorescently marked and introduced into porous polymers of the Fluoropor type. The spreading of the water inside the pores will be tracked by fluorescence microscopy in 2D and by confocal microscopy in 3D to provide experimental insights into the spreading dynamics. We will assess, if such models are useful for predicting substrate properties such as pore sizes from spreading data by applying a fitting theoretical model.

Structuring of polymer surfaces – collaboration with Prof. Frank A. Müller (Otto-Schott Institute, Friedrich-Schiller University, Jena)

LIPSS are a versatile tool for generating micron-sized structures in metals, glasses or polymers [76]. As shown by Prof. Müller, the periodic structures generated resemble naturally occurring surfaces and can mimic, i.e. gecko feet, insect or plant skins [54]. In this collaboration, the porous, spiropyran-containing polymers provided in this project, will be structured by LiPSS to introduce a second topography hierarchy. The nano-/micropores of Fluoropor will serve as the underlying hierarchy, while the periodic structures induced by the laser will serve as the second hierarchy. This will be used to increase the contact angle by stabilizing the Cassie wetting regime on the polymer foam. Different periodic structures will be tested to evaluate the highest possible contact angle. This elevation of the contact angle size by surface structuring will help to improve the difference between contact angles of switched spiropyran states.

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4. Requested modules/funds

4.1. Funding for staff (DFG form 52.01 / II.1)

The scientific work packages will be performed by a PhD student (75 % TVL-13, as recommended by the coordinators). This work will also be supported by a student assistant, who will also help the PhD to generate hands-on tutorials that shall facilitate training in advanced techniques (PDF training course for future students and the public). The personnel rates according to the DFG (form 60.12) for 100% E13 PhD students (64.500 €) and student assistants at the University of Freiburg (42 h per month at 10,01 € per hour, therefore 420,42 € per month and 5045,04 € per year) are the foundation for the following calculation.

Personnel	Year 1	Year 2	Year 3
PhD student (doctoral researcher, according to DFG forms 60.12, 55.02)	48.375 €	48.375 €	48.375 €
Student assistant	5.054 €	5.054 €	5.054 €
Sum	53.429 €	53.429 €	53.429 €
Sum (3 years)	160.287 €		

4.2. Funding for direct project costs (DFG form 52.01 / II.2)

Travel calculations are based on the recommendations by the coordinators, 80 € per person per day for accommodation and subsistence, 200 € per person for travel in Germany. International travel per Person: 1.000 €, conference fee per person: 600 €.

Item	Year 1	Year 2	Year 3
<i>Equipment, software and consumables (see DFG form 52.01 / II.2.1)</i>			
General lab consumables (pipettes, glasware for chemical synthesis, gloves, syringes, etc.)	1.500 €	1.500 €	1.500 €
Chemicals for SP synthesis (mono- and bifunctional, reagents for introducing functional groups)	3.000 €	3.000 €	3.000 €
Monomers (fluorinated, non-fluorinated acrylates)	2.000 €	2.000 €	2.000 €

Chemicals (solvents, washing, gelation, porogens, acids, fluorophores, initiators)	1.500 €	1.500 €	1.500 €
High speed colour camera	3.200 €	0 €	0 €
Software (shape tracking, camera data acquisition)	2.000 €	0 €	0 €
Sum	13.200 €	8.000 €	8.000 €
Sum (3 years)	29.200 €		
Travel (see DFG form 52.01 / II.2.2)			
SPP workshop (PI + PhD), 4 days	1.040 €	1.040 €	0 €
Advanced School (PhD), 5 days	600 €	0 €	0 €
PhD workshop (PhD), 4 days	0 €	520 €	0 €
International conference (PI + PhD), 5 days	0 €	0 €	4.000 €
Regular meetings between collaborators	300 €	300 €	300 €
Sum	1.940 €	1.860 €	4.300 €
Sum (3 years)	8.100 €		
Project-related publication expenses (see DFG form 52.01 / II.2.6)			
Publication expenses (open access, color images, title pages, etc.)	750 €	750 €	750 €
Sum	750 €	750 €	750 €
Sum (3 years)	2.250 €		
Total direct project costs			
Sum	15.890 €	10.610 €	13.050 €
Sum (3 years)	39.550 €		

5. Project requirements

5.1. Employment status information

Helmer, Dorothea, Dr. Postdoc at the group of Prof. Bastian Rapp, Department of Microsystem Technology (IMTEK), University of Freiburg, permanent position.

5.2. First-time proposal data

Helmer, Dorothea. The applicant has never before applied for DFG or any other funds.

5.3. Composition of the project group

Dr. Dorothea Helmer, permanent contract (financed by IMTEK) will supervise the project. Dr. Helmer has expertise in organic chemistry (Diploma + PhD), functional coatings, coating characterization, super-repellent surfaces, polymer chemistry, microstructuring and lithography (postdoc).

The project will be embedded in the group of Prof. Bastian E. Rapp which is an interdisciplinary work group spanning expertise from classical microsystem engineering, material science and organic chemistry all the way to application development and technology development. Prof. Rapp will act as advisor to this project. The project will have access to all technologies and instrumentation established in the group as well as the hosting institution (IMTEK). This includes the use of standard equipment such as contact angle measurement systems and microscopes as well as custom-made instrumentation and software such as the DMD-based photolithography set-up. The development of the imaging platform (WP4-1 and 4-2) that will require the installation of high-speed cameras in this system is explicitly supported by Prof. Rapp. Prof Rapp has developed the control software for the lithography set-up and has agreed in helping to develop a novel software for the operation of the imaging platform. Additionally, a student assistant with background in programming will be hired (see below). The LED Displays for photoswitching will also be provided by Prof Rapp.

The newly founded mechanical fabrication centre at IMTEK enables the fast and convenient fabrication of customized parts for the development of novel instrumentation which will help in building the imaging platform. In terms of chemical synthesis, Prof Rapp will provide a workspace in a chemical lab equipped with a fume hood as well as room for proper storage of chemicals. Prof Rapp will also provide access to a fluorescence microscope for the analysis of droplet spreading in porous materials (WP4-5).

Tobias Nargang (PhD) is the group expert on surface functionalization “BioBitmaps” and will be available for the course of this project to help and give advice concerning the coating technique and operation of the machine. Tobias Nargang will not be paid by this project.

Frederik Kotz (Postdoc) is an expert on mechanical engineering and technology development. He has built a microstereolithography machine based on the DMD-based photolithography setup and will help to install and operate the imaging platform for droplet analysis. Frederik will not be paid by this project.

A PhD student and a student assistant will be acquired at the university of Freiburg. The PhD should have a strong chemical background ideally with basic experiences in polymer chemistry. The research assistant should be experienced in programming and informatics to help with the operation of the imaging platform and the development of internet tutorials. PhD and student assistant will be involved in group seminars at the group of Prof Rapp to ensure an interdisciplinary training.

5.4. Cooperation with other researchers

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

For researchers collaborating within the SPP please see 2.8. Additionally, we have agreed on the following collaboration:

Electrokinetically driven surface deformations (EDSD) – Associate Prof. Moran Bercovici (Technion, Israel)

The forces acting at the 3PCL induce the formation of a wetting ridge on soft substrates (see Figure 3). Additionally, capillary forces can lead to surface deformation, thus causing, e.g. the self-assembly of microscopic and even millimetre-scale self-assembly, sometimes referred to as “capillary-origami” [77, 78, 79]. Bercovici et al. concluded in their recent theoretical work that the pressure of a liquid can be used to exert force on a soft (elastic) surface to generate reversibly changeable surface deformations [71]. On a surface with changeable surface charges, such deformations should be controllable and could be used to create, i.e., virtual channel geometries in real time. The SP switch results in a charged MC molecule and thus switched surfaces are expected to show a significant change in surface charge. Combined with a thin-film of polymer or gel, the SP surfaces created in this project could be used for ESDS. The ESDS mechanism of reversibly switching surface topographies is an interesting approach for switching a surface between Cassie and Wenzel states, by, e.g. introducing dynamic structures, such as posts or bumps to analyse the effect on the 3PCL behaviour. Within this collaboration, we will develop surfaces suitable for ESDS and evaluate their possibility for dynamic topography switching.

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

KIT: Gary Davidson, Uwe Strähle, Kerstin Länge, Christof Niemeyer, Jürgen Hubbuch, Matthias Worgull, Nicolas Foulkes, Pavel Levkin, Steffen Scholpp, Matthias Franzreb, Olivier Kassel, Werner Bauer, Dieter Schield, Christian Greiner, Thomas Schwartz

External: Bonnie Gray (Simon Frasier Canada), Motomu Tanaka (U Heidelberg), Collin Sones (U Southampton), Edgar Sánchez-Sinencio (TAMU), Stefan Giselbrecht (U Maastricht), Roman Truckenmüller (MERLN University of Maastricht); Wolfgang Wiechert

(Research Center Jülich), Andreas Manz (KIST), Paul D. Dalton (U Wuerzburg), Andrew deMello (ETH Zuerich), Katja Schmitz, Rolf Jakoby (TU Darmstadt)

Industry: Klaus Stoll, Wolfgang Schrof, André Fuchs (BASF); Victor Keasler, Renato DePaulo (Ecolab), Michael Thiel (Nanoscribe)

5.5. Scientific equipment

IMTEK provides resources for PC infrastructure, telephone, office supplies, energy costs and software licenses for standard programs and instrumentation, which do not have to be covered by the applied project.

Technological facilities: organic synthesis laboratory for polymer synthesis, UV-lamps, maskless projection lithography system, LED Displays, contact angle measurement station with roll-off setup and highspeed camera, optical microscopes, fluorescence microscope, rheometer, confocal microscope, UV/VIS Spectrometer, NMR spectrometer for substance characterization.

5.6. Project-relevant cooperation with commercial enterprises [not applicable]

5.7. Project-relevant participation in commercial enterprises [not applicable]

6. Additional Information [not applicable]