

Project Description

AzoDune: Light switchable dynamic wetting on azobenzene containing structured polymer surfaces

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1. State of the art and preliminary work

It is well known that the wetting properties of solid surfaces crucially depend on two key parameters, i.e. surface energy and roughness [1-3]. Understanding the wettability on solid surfaces is related to many significant technological and industrial applications, including lubrication, coating, printing, waterproofing, self-cleaning, and microfluidics. For perfectly smooth, chemically homogeneous, rigid, insoluble, and nonreactive surfaces, the wetting characteristics are defined as a function of the interfacial free energies. However, most of the real surfaces existing in nature, or fabricated by different technologies are rough and/or chemically heterogeneous. The contact angle of a sessile liquid drop on a rough surface is determined by the geometrical parameters of the texture such as liquid-solid contact areas, and is usually described by the thermodynamic models of Wenzel and Cassie and Baxter [4-9]. In case of complex surface topographies exhibiting for instance, sharp edges [10-12], asymmetric textures [13-17], or re-entrant surface curvatures, a great variety of complex wetting phenomena have recently been reported such as anisotropic and unidirectional liquid spreading (asymmetric textures) [18-22], or omniphobicity [23,24], and many others. In all these examples the wettability characteristics are intimately related to the fabrication of complex surface topographies and textures. Typically, structured surfaces for wettability studies are designed using standard techniques such as soft lithography, photolithography or electron and ion beam lithography [25-27]. Using these approaches it is possible to create textures of different shapes, sizes and periodicities. The materials used for production of periodic patterns are usually PDMS based because of its simple handling and cross-linking. The resulting structured surfaces are, however, static with respect to shape and hence wettability properties. This is of course indispensable to achieve long term stability, on the other hand in many cases it might be desired to study and design wetting phenomena related to dynamically changing surfaces that can be realized by applying external stimuli including heat, electric fields, and light. The creation and tailoring of reversibly programmable surfaces is also of great practical interest for moving and handling small amounts of liquid in micrometer dimensions such as microfluidic chambers, channels or surfaces that act as microarrays for droplet deposition and screening. Manipulation of liquid droplets by simple external mechanical intervention (e.g. pipettes) is extraordinarily difficult because surface tension effects dominate on micrometer length scales. So it appears as a viable strategy to control the wetting properties instead.

Generally, a surface with configurable wettability can be created by modifying hierarchical micro/nanostructures with responsive molecules to arrive at various smart wetting phenomena such as reversible transitions between a superhydrophobic and superhydrophilic state and high/low adhesion; external stimuli suited to trigger these transitions can be temperature, pH, light and so on [28-32]. Photo-switchable surfaces offer the additional feature of distinct spatial heterogeneity in order to manipulate liquid droplets by corresponding patterns of wettability; light as an external stimulus is particularly simple to tune and to control. One of the strategies to render a surface photoresponsive is to modify it with photoreactive groups among which azobenzenes are the most common. There were several reports on using azobenzene molecules to tune the wettability of surfaces by light [33-38]. Usually the azobenzene molecules are used to form a self-assembled monolayer on a solid surface; changes in surface energy and thus wettability are directly related to corresponding changes of the azobenzene moieties under the reversible transitions between their isomers, because *trans* and *cis* states exhibit different dipole moments and thus hydrophobicities. Using this approach it was shown that one can induce motion of a water droplet to regions of higher surface energy where the azobenzenes were mostly in their *cis*-state [39]. However, the change in wettability using such a surface energy based strategy leads to changes in contact angle only between 5° and 20° while the contact angle was always below 90°. Thus, flat azobenzene modified surfaces are restricted to non-hydrophobic phenomenology. On the other hand, anisotropic behaviour of the water droplets on sinusoidally varying topographies and textures made from arrays of posts involving azobenzene containing polymers have also recently been reported [40,41]. Still all of these approaches rely on the variation in surface chemistry or topographic microstructures both of which are static, in other words, the surfaces thus prepared only offer a global on/off functionality excluding “smart” phenomena such as directional adhesion [42], water collection [43,44], and water directional spreading [45,46].

Although the great potential of light induced switching of surface topographies has clearly been recognized, there are no studies till now showing that changes in topographies and hence wettability can also be achieved in a local, dynamical and reversible manner. This could lead to the ultimate application of a programmable workbench for manipulating and operating an ensemble of droplets, just by using simple and gentle optical stimuli.

In this project we are going to lay down the foundations for such a vision. In particular, we are combining reversible texture changes in azobenzene containing thin polymer films, structured polymer surfaces made from arrays of posts, pillars and lines, with accurate control of local illumination conditions with respect to light intensity and state of polarization. For instance, a relief from an interference pattern can not only made to appear or disappear, we will also be able to make it wander like dunes in a desert.

Preliminary work

The general focus of our work is on fundamental phenomena of soft matter at surfaces and interfaces and on the interactions between nano-particles and nano-structured polymer surfaces. In a series of articles we reported for the first time on how nano-particles adsorbed on a polymer brush can be moved without the need of external mechanical intervention [47, 59, 60]. This

research was motivated by our quest for alternatives to the slow process of using AFM for such purposes. In our approach, the objects are moved due to the dynamical fluctuations in morphology changes of polymer films they are adsorbed to: under suitable conditions, polymer brushes show a so-called nano phase separation causing the changes in morphology [48,49], varying on a nanometer length scale and occurring during phase transitions induced by changes in environmental conditions [50]. Quite intriguingly, we could show the particles remain firmly adsorbed at any stage during the phase separation process; in a way, they are gradually passed from one local structural feature of the phase separated polymer material to an emerging one in the immediate neighborhood [47].

Starting from our research on polymer brushes [P2, P3], we ever since sought for more convenient external stimuli to induce fluctuations in polymer film topography. At the moment, we are following three very different strategies: (i) remote control of nano-phase separation [47], (ii) actuation of magnetic particles immersed in thin polymer membranes with magnetic fields [51], and a recently developed approach (iii) exploiting light driven topography changes in photosensitive polymer films [52, P1]. **In this project we plan to utilize exclusively photosensitive polymer films.**

To make polymer films photoresponsive, we integrated azobenzene molecules as side groups into the polymer chains (**Figure 1a**).

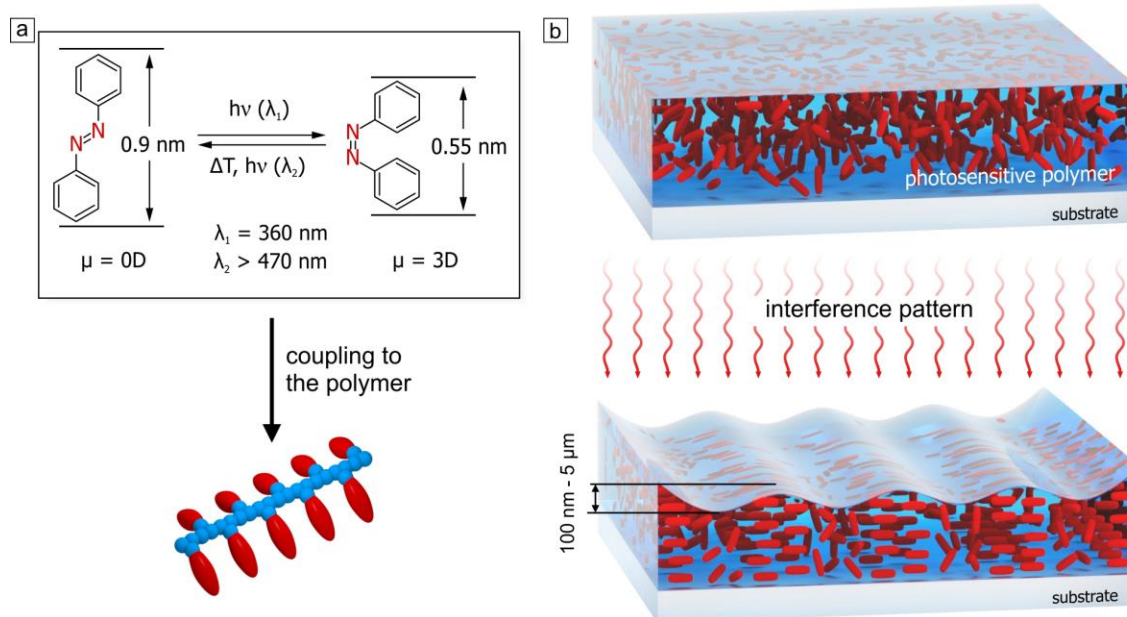


Figure 1. (a) Schematic of an azobenzene molecule and its characteristic properties in *trans*- and *cis*- states. To make a polymer photosensitive, these moieties are introduced into its side chains. (b) Within a photosensitive polymer film, morphological changes are induced by the formation of different phases related to the azobenzene containing side groups. The orientation of the latter is determined by the direction of local polarization.

Azobenzene, consisting of two phenyl rings linked by an azo group ($N=N$), can undergo reversible photo-isomerization between a more stable *trans* and a metastable *cis* conformation during illumination with light of appropriate wavelength in the UV- to visible frequency range. The

photo-isomerization reaction involving azobenzene is completely reversible and one of the cleanest photoreactions known, without any byproducts. Along with the conformational changes, the physical properties of the molecules are also altered: their shape switches from rod-like to "Γ-like" with a corresponding increase in free volume, the dipole moment increases from 0 Debye in the *trans* to ~3 Debye in the *cis* conformation. When integrated into a polymer chain, the photo-isomerization changes the properties of the polymer material as a whole, possibly over many length scales. One very remarkable effect can be achieved when an azobenzene containing thin polymer film is irradiated with an interference pattern, that is, a spatially and periodically varying irradiation field (**Figure 1b**). Under these conditions the polymer topography deforms following the local distribution of the electrical field vector. The topography pattern then simply mimics the interference pattern and forms a sinusoidally shaped feature of periodicity equal to the optical periodicity. One remarkable fact about this process is the state of the polymer: it remains glassy all the times without intermediate softening, the mechanical properties of the polymer substrate are largely preserved. The extent of the deformations may be considerable, local differences in height can be of the order to the total film thickness, i.e. up to several micrometers. The mechanism of the photo-mechanical deformation is related to the generation of internal opto-mechanical stresses. The process on the molecular level can be viewed as follows: under irradiation inducing cyclic *trans-cis-trans* isomerization, the azobenzene molecules rotate and re-orient perpendicularly to the electrical field vector, indicated schematically in **Figure 1b**. This redistribution of the azobenzenes causes a re-orientation of the polymer backbones to which the azobenzenes are attached, and thus a macroscopic deformation of a sample due to strong mechanical coupling between the two phases: active azobenzene molecules and a passive polymer matrix [53].

Although the phenomenon of SRG formation has been known for more than 20 years, at the time we entered this field there were two fundamental open questions. For instance, one might be interested in how strong the stresses generated within the polymer film are during SRG formation, given that the material must be deformed in a solid-like state. We were able to measure these stresses experimentally and showed that they must be as high as 1GPa, while the intensity of irradiation is rather low (50mW/cm²). This inspired our collaborator (Ref. 53) to suggest the orientational mechanism described above. From the general point of view the strong optomechanical stresses developed in the polymer means that it should be able to do work on objects or other materials adsorbed on top. For instance, a deposited metal layer can easily be ruptured [54,55], an adsorbed graphene layer can be strained up to several percent [56]. The second fundamental question was how to relate the local variation of topography to that of the electric field vector. In order to gain insight into this question we have invented a versatile reliable method, creating a home-made *in-situ* interferometric AFM setup to study the change in polymer topography in real time during switching between different interference patterns (**Figure 2a**) [57, P5]. With this setup we were able to identify the orientation of the electric field vector \vec{E} as a function of position along the surface relief gratings for all possible polarization combinations of two interfering beams (**Figure 2b**) [58, P4]. Simultaneously with the spatial distribution of \vec{E} , it is possible to record the topography change *in situ*. **Figures 2d-f** show the change in topography of three different polymer films during switching the polarization of the interference pattern, in this case a change from intensity to polarization modulation combinations (from PP to ± 45 and back to PP).

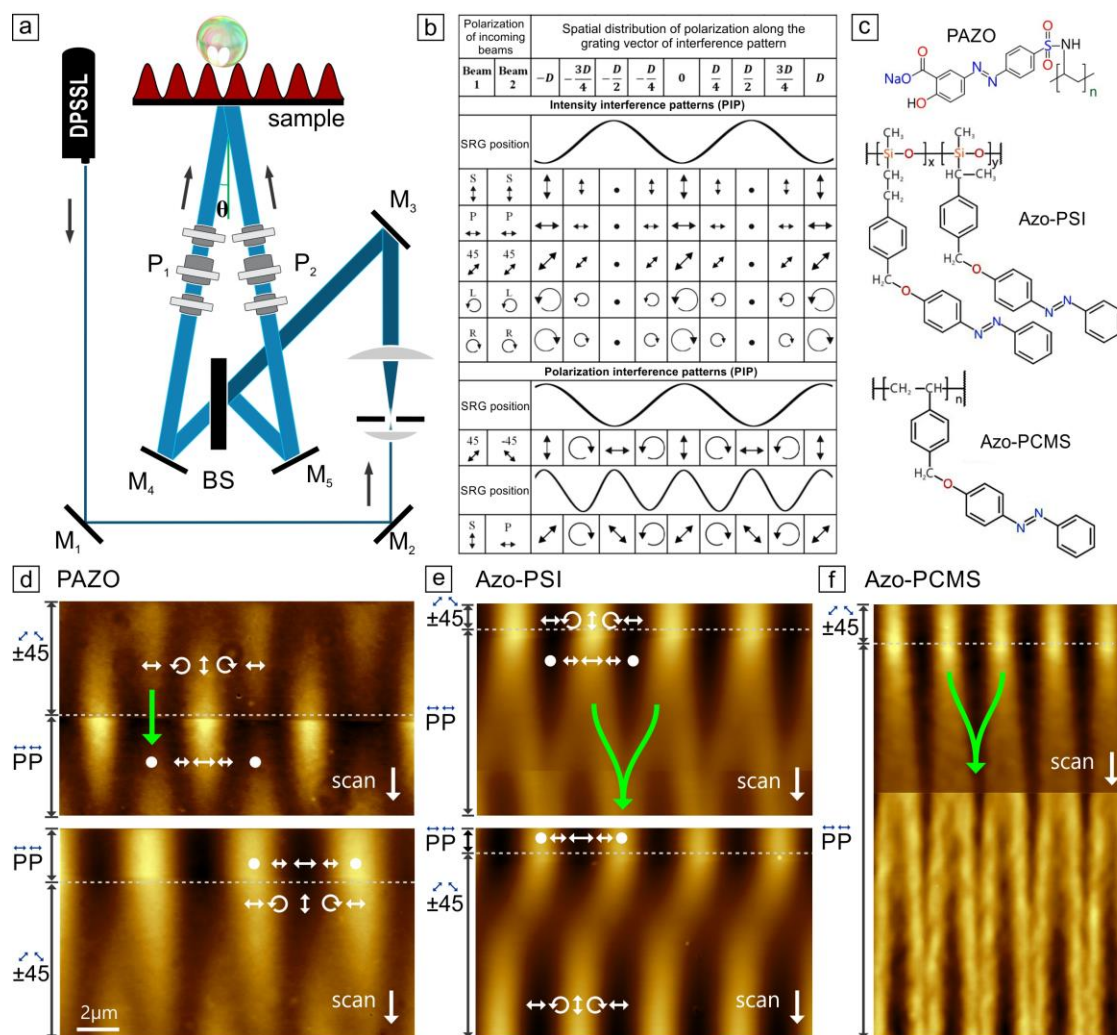


Figure 2. (a) Scheme of the home-made set-up combining an optical part (two- or three-beam interference lithography) and microscopes (both, AFM and/or optical microscope). Using this setup one can simultaneously irradiate a photoresponsive polymer surface (schematically shown in red) and acquire its topographical changes as well as the shape and position of a deposited colloid or liquid droplet. (b) Examples of different interference patterns (IPs) either with periodically varying intensity (intensity interference patterns, IIPs), or with constant intensity, but different local distribution of electrical field vector indicated by the black arrows in the table, (polarization interference patterns, PIPs). The IPs are generated by changing the polarization of two interfering beams (Beam 1 and 2). The local distribution of the electrical field vector is shown for one optical period, which can be adjusted roughly between 250nm and 10 μ m. (c) Examples of the chemical structures of azobenzene containing polymers. (d-f) AFM micrographs of three different photo-responsive azobenzene containing polymers exposed repetitively to different interference patterns annotated symbolically to the left of the each micrograph. The local distribution of the electrical field vector is indicated by the white arrows. The scan direction is from top to bottom. When the IP is changed, the surface relief grating (SRG) formed changes following the distribution of the electrical field vector. This results in the dynamic variation of the polymer topography. Depending on the polymer, one may obtain different “wave form” patterns (compare Figures 2d, e and f). Irradiation intensity is 50mW/cm²; wavelength $\lambda=491$ nm.

The corresponding distribution of the electrical field vectors \vec{E} is depicted in the figure as well. For instance (**Figure 2f**), the topography maxima emerging during $\pm 45^\circ$ irradiation split into two after switching the PP polarization combination. For other polymer, the topography maxima split and then travel to the left (**Figure 2e**).

In general, the AFM micrographs prove that the grating migrates as a whole, resembling the motion of dunes in the desert. **In other words, we induce a traveling topographical wave train within a solid polymer film with rather gentle optical stimuli.** The virtues of our setup are that the dynamics of polymer film fluctuations can be controlled not only spatially but also temporally. One may stop migration at some point and resume at a desired later time just by switching light on and off.

Recently we were able to show (unpublished results) that similar changes in shape and topography can be induced in rather small isolated posts of azobenzene containing polymer. For instance, in **Figures 3 and 4** we display a gallery of different shapes that have been inscribed into a polymer posts (**Figure 3**) or stripes (**Figure 4**). Depending on the nature of the interference pattern applied, that is, different local distributions of the electric field vector (shown as black/white arrows in **Figure 3**), one can obtain a variety of peculiar shapes. As in the case of films, these shape changes can be reversed.

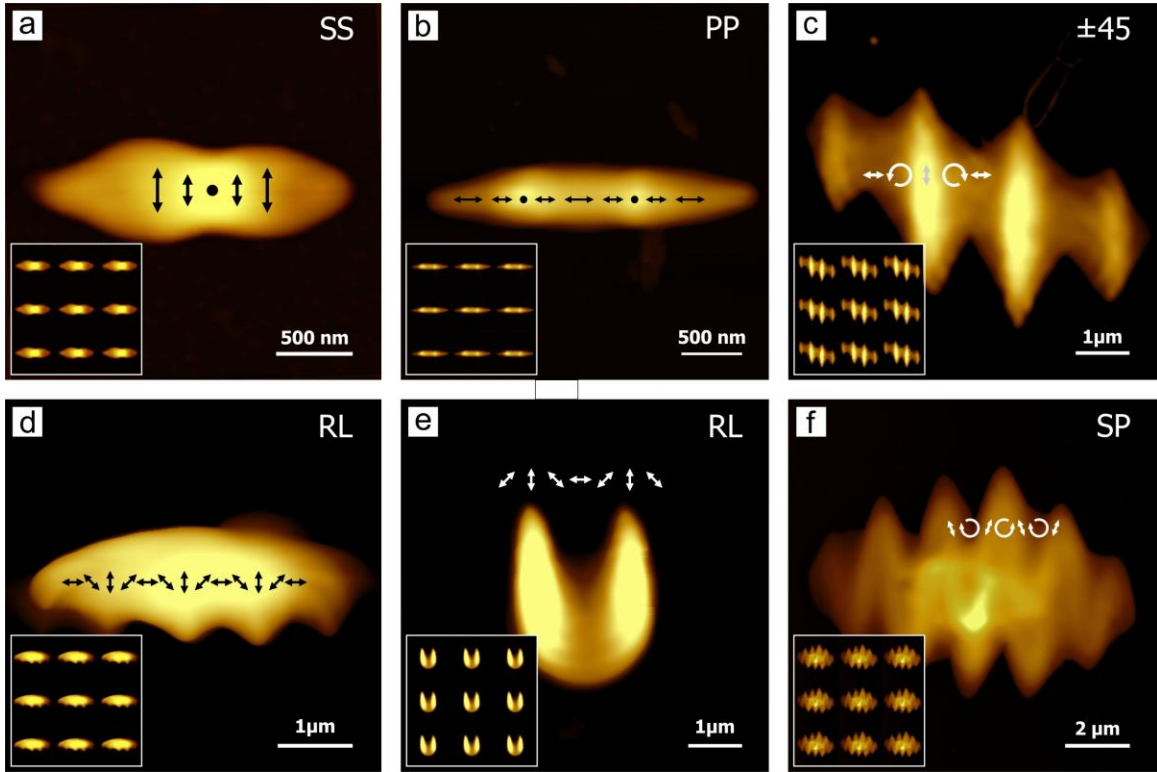


Figure 3. Subfigures (a-f) show different deformations of the same polymer post under varying polarization conditions (SS, PP, $\pm 45^\circ$, RL, SP) of the interfering beams. The insets show an extended region of 9 posts from the same array. The black/white arrows indicate local distribution of the electrical field vector relative to the topography pattern. The posts are made of azobenzene containing polymer (PAZO, see Figure 2c for chemical structure). Irradiation intensity is 50 mW/cm^2 ; wavelength $\lambda = 491 \text{ nm}$.

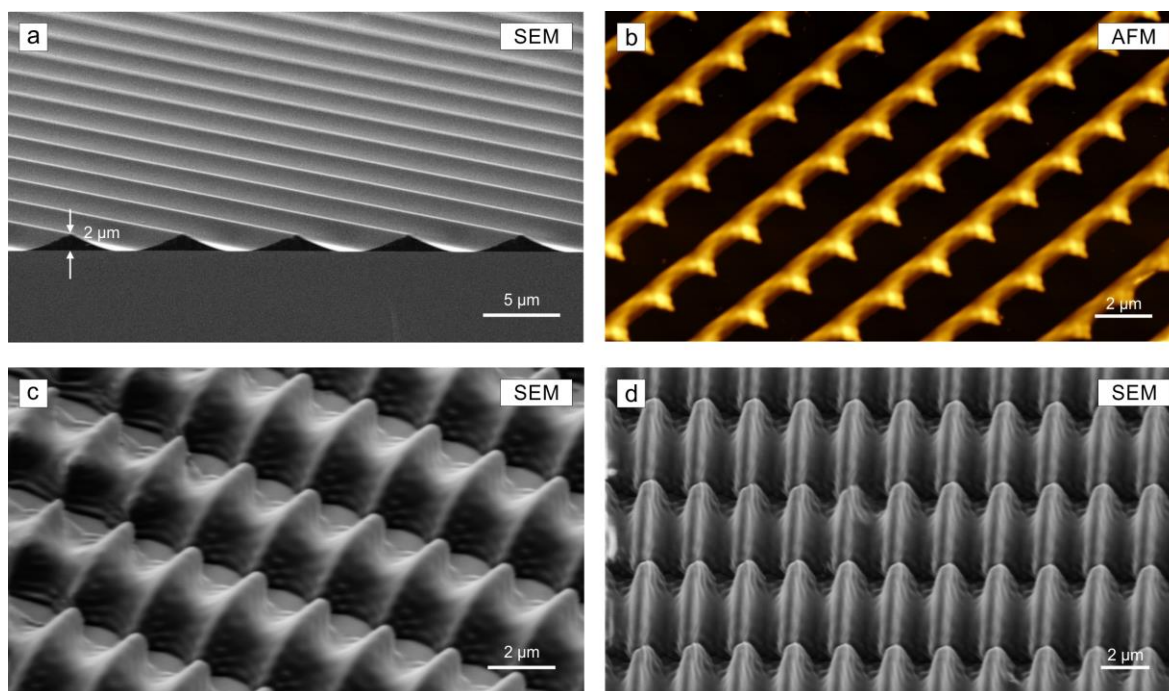


Figure 4. SEM/AFM micrographs (a-d) show the modulation of an array of lines of photosensitive polymer (PAZO, see Figure 2c) by various interference patterns: (a) initial (before irradiation) pyramid like polymer stripes, (b) AFM micrograph of the stripes after irradiation with RL interference pattern. (c-d) SEM micrographs show the stripes after irradiation with $\pm 45^\circ$ interference pattern for 2 minutes (c) and 5 minutes (d). Irradiation intensity is 50 mW/cm^2 ; wavelength $\lambda = 491 \text{ nm}$.

We should emphasize that we can control the distribution of the direction of electric field vector such that a change in polarization states will lead to defined response in the polymer film with high spatial and temporal precision. **In this way the generation of dynamically fluctuating topographies induced by light can be realized in a defined way. In this project we shall exploit this effect to induce migrating or fluctuating patterns in various types of structured surfaces made of photosensitive polymers in order to create and study light induced dynamic wetting.**

List of project-related publications

- P1. Yadavalli, N. S.; Loebner, S.; Papke, Th.; Sava, E.; Hurduc, N.; Santer, S. A comparative study of photoinduced deformation in azobenzene containing polymer films, *Soft Matter*, 12 (2016) 2593-2603.
- P2. Kopyshev, A.; Galvin, C.J.; Patil, R.R.; Genzer, J.; Lomadze, N.; Feldmann, D.; Zakrevski, J.; Santer, S. Light-induced reversible change of roughness and thickness of photosensitive polymer brushes, *ACS Applied Materials & Interfaces*, 8 (2016) 19175–19184 .
- P3. Kopyshev, A.; Galvin, C.J.; Genzer, J.; Lomadze, N.; Santer, S. Polymer brushes modified by photosensitive azobenzene containing polyamines, *Polymer*, 98 (2016) 421.

- P4. Yadavalli, N.S.; Saphiannikova, M.; Santer, S. *Photosensitive response of azobenzene containing films towards pure intensity or polarization interference patterns*, Appl. Phys. Lett., 105 (2014) 051601.
- P5. Yadavalli, N. S.; Saphiannikova, M.; Lomadze, N.; Goldenberg, L. M.; Santer, S. *Structuring of photosensitive material below diffraction limit using far field irradiation*, Applied Physics A, 113 (2013) 263–272.

2. Objectives and work program

2.1 Anticipated total duration of the project

The project's intended duration is 36 months.

2.2 Objectives

In this project we are going to create a photoresponsive, structured surface with locally adaptable wetting properties for manipulation of liquid droplets. The unique features of our approach are that the changes in wetting properties can be triggered just by application of soft optical stimuli, which lead to dynamical, reversible changes in the local morphology of the structured surfaces. In order to achieve this, we are going to exploit the unique properties of azobenzene containing polymers to create patterned surfaces. The structured surfaces will consist of patterns of lines, posts, pillars and other shapes to render them hydrophobic in the beginning (**Figure 5**).

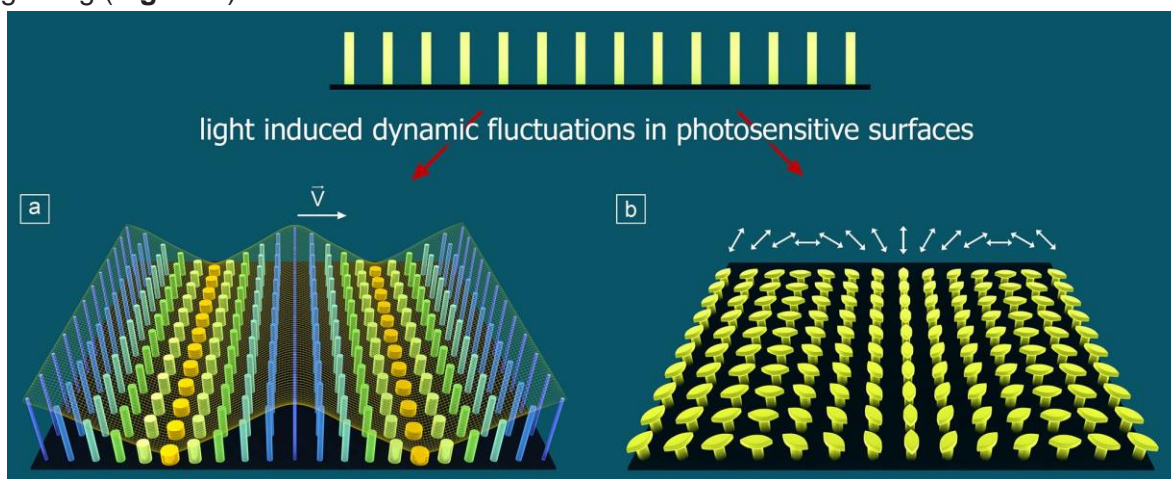


Figure 5. Scheme of light induced dynamic fluctuations in photosensitive polymer substrates. In the example shown the surfaces consist of photosensitive polymer posts (schematic above (a, b)). (a) By applying periodic polarization changes in an interference pattern impinging onto an array of posts, the change in shape can be made to propagate as a wave train across the substrate. Different colors of the posts indicate different surface energy. At the topography minima (yellow color) the light intensity is at maximum, and thus the surface energy is larger due to *trans-cis* isomerization. With an adequate tuning of the periodicity of the wave train, one may effect also a continuous transport of an adsorbed liquid droplet by pinning its contact line in “valleys”. (b) Spatial variation of preferred wetting directions, by applying a rotating local distribution of the electrical field vector (schematically depicted by white arrows). This pattern may be made to propagate as well.

The expected changes in wetting properties can be generated by deforming single, small amounts of photosensitive polymer (a single pillar, for instance). The extent to which this is possible and what shape deformations are possible are indeed quite fundamental questions that have not been addressed so far; our preliminary work summarized in **Figures 3** and **4** only give a first impression. Upon SRG formation in extended thin azobenzene containing polymer films, the polymer can flow or deform over large distances, but with finite-size posts we may have to refine our conceptual picture: in order to make topographies and thus wetting characteristics vary over distances larger than the size of a single pillar, the extent to which it can be deformed must adapt accordingly. From these considerations and based on our preliminary work we suggest two types of operation modes. The first one is geared at changing the size and shape of single posts to achieve changes in hydrophobicity or to induce anisotropic wetting properties. This shall be referred to in the following as the “shape” mode. The second mode is related to modifying the properties of the contact area of single structural elements they have in common with an adsorbed liquid droplet. Contact area modification can be achieved by, e.g., imprinting an SRG on top of a pillar, affecting only its topmost layer of polymer material. This is referred to as the “print” mode. With both modes, dynamically fluctuating patterns on length scales larger than that of single pillar, line or post or any other structural element shall be created in order to generate propagating areas of varying hydrophobicity, triggered by periodic polarization changes in an interference pattern impinging onto the structured surface.

For the case of the shape mode, **Figure 5** illustrates the two possible scenarios for global spatio-temporal variations. **Figure 5a** shows a pattern that is supposed to travel in a wave like fashion to eventually drag liquid droplets into a preferred direction. The second dynamical pattern is characterized by anisotropic wetting that may be used to rearrange adsorbed droplets or change their shape, e.g., from spherical to elongated, see **Figure 5b** for an example.

The ultimate goal is then to find an optimal combination of designed interference patterns and suitably pre-structured polymer surfaces to achieve the most pronounced light controlled dynamic wetting. We emphasize that for completeness, not only meta-structuring will be considered (interference patterns acting on arrays of structural elements), but also the topographies that can already be achieved with continuous thin polymer films as shown in **Figure 2**.

2.3 Work program including proposed research methods

According to our objectives, the work plan divides into two parts. In the first part comprising the major body of work, in order to achieve a spatial variation of hydrophobicity, the shape mode will be addressed that is, we will consider arrays of structural elements the shape of which is expected to change in a dynamic and reversible way by applying an optical stimulus. In the second part we will focus on several possibilities to realize the print mode. In addition to using the imprint of SRGs into extended posts, we shall also consider azobenzene containing, liquid crystalline polymers, with which desired changes in hydrophobicity but especially in anisotropy of wetting properties can be achieved.

The project comprises four work packages: the work schedule is planned for one PhD student for three years who will take care of the experimental study and actively participate in discussions with theoretical groups of Prof. H. Stark and furthermore Prof. M. Oettel and Prof. R. Stannarius.

WP1. Generation of structured arrays of photosensitive material and characterization of response under irradiation with different interference patterns.

The starting point of the project will be to establish a procedure to create a variety of different surface structures such as arrays of lines, posts, pillars etc. made of azobenzene containing polymers. Here we will apply a soft lithography procedure by which a thin polymer film is created with a suitably structured matrix such as a PDMS stamp. We should mention that the PDMS stamp with the required texture will also be produced using azobenzene containing polymer films: in a first step we will irradiate thin azobenzene polymer films with interference patterns resulting from two or three beam interference lithography to generate surface relief gratings of different shapes and sizes. With this method it is possible to vary the periodicity of the pattern between 200nm and 20 μ m, (the desired size of single posts that make up a hydrophobic array falls into a similar range). The structured polymer film is in a stable, solid state and further serves as a positive by which a negative mask from PDMS will be generated. This way, we can make double use of our interference beam lithography setup and the azobenzene material. Note that the detour via an PDMS mask is necessary to arrive at the desired pattern of isolated elements (lines, posts, pillars, ...) with no polymer in between. This situation cannot be achieved with SRG formation alone. The resulting structures will be characterized comprehensively by electron microscopy and AFM.

We note that for the resulting functional surfaces, their wetting behavior is governed by two parameters, surface energy and surface texture (for instance, periodicity of pillars). We can expect that a variation in surface energy should occur, which is related to changes in physico-chemical properties of the azobenzene moieties under *trans-cis* isomerization. In **Figure 5a** we colored posts to indicate differences in surface energy due to differences in the extent of *trans-cis* isomerization. Indeed, the topography minima are typically formed at the intensity maxima in amorphous azobenzene containing polymers. Therefore at these locations (topography minima) more azobenzenes are isomerized from *trans* to *cis* resulting in an increase of surface energy. For instance, for a so-called push-pull azobenzene molecule with electron withdrawing and donating ring substituents the change in dipole moment (and thus the hydrophobicity) can be as large as 9 Debye per molecule, certainly resulting in an overall change in surface energy under irradiation. We therefore need to characterize comprehensively the relative contributions from surface energy changes (type of azobenzene molecule) and change in texture (topography), starting with a sufficiently simple test system such as a flat polymer film under homogeneous irradiation and a corresponding array of posts that will add the feature of texture change. In combination with an analysis of shape changes of single structural elements and a variation of the nature of the azobenzene side chains a series of measurements assessing wettability will be conducted. In addition, we will consider the use of liquid crystalline azobenzene containing polymer materials. An example of the chemical structure of such a polymer is shown in **Figure 8b**.

WP2. Light induced dynamic fluctuations in arrays of structural elements (shape mode).

Recall that in our preliminary work we have shown that the SRG in a polymer film can be made to travel as a propagating wave by temporally changing the polarization conditions of two interfering beams. This was possible because under the conditions described shape changes are completely reversible. This is not so obvious in the case of an isolated piece of polymer

material. The major challenge in this WP is to arrive at operation conditions with respect to irradiation time, intensity, periodicity of the texture and the local distribution of the electric field vector to facilitate reversible shape changes for isolated posts as well. For this a few technical changes to our experimental set up have to be made that most importantly involve a change in irradiation direction. In our conventional SRG experiments, the film is illuminated “from below”, that is, the radiation penetrates the supporting solid substrate first.

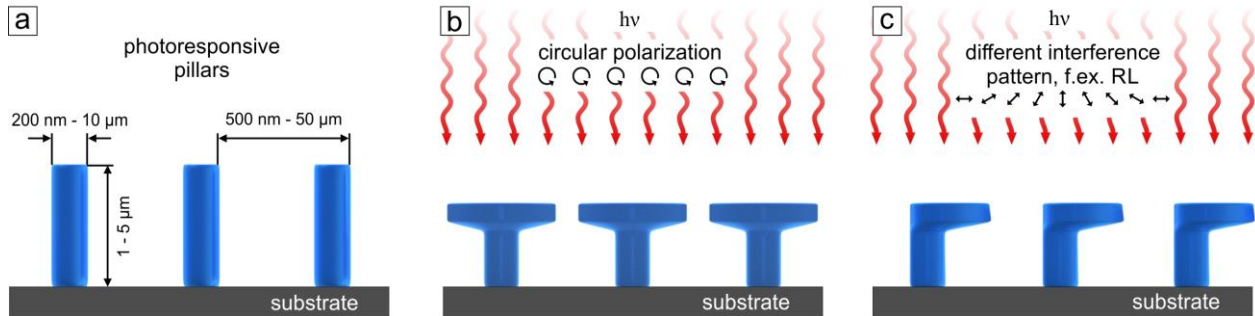


Figure 6. Scheme of the photosensitive posts made of azobenzene containing polymer material (blue color): (a) shows the possible size, height and periodicity of the posts, (b-c) depending on irradiation interference pattern different deformations of the posts can be achieved.

We will, however, need to establish irradiation from above as well, for the following reason. We expect that in both cases the deformation of single posts or pillars achieved could be very different. In the “from below” configuration, mainly a flattening of the whole pillar can be expected, whereas in the “from above” situation only the top most part of the pillar will be affected due to the limited penetration depth of the radiation. In this case we expect a mushroom-like deformation of the pillars, see **Figure 6**.

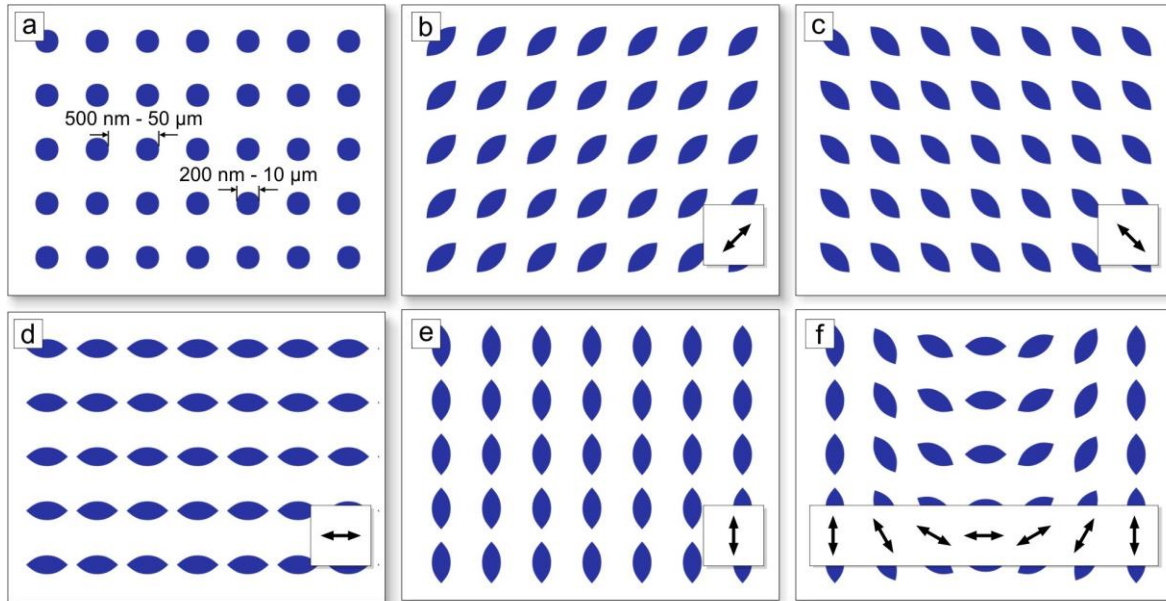


Figure 7. 2D illustration of the structured surface. Depending on the direction of the light polarization different pattern can be inscribed within the array. The electrical field vector is depicted in each scheme by black arrow.

The crucial aspect here is that the structure and shape of the pillars close to the solid support remains intact and only the topmost part is subject to shape changes. This will guarantee the reversibility of the process because the polymer material cannot spread across the solid support producing, for instance, a strongly adhering pancake structure. Depending on the polarization direction and polarization distribution of the incoming irradiation, different possibly asymmetric patterns can be induced within single pillars such that the array as a whole develops preferential directions with respect to which changes in wetting properties occur. For instance in **Figure 7** we sketch a scenario in which the topmost portion of a pillar is distorted into an ellipsoidal shape with a global direction. If in addition the distribution of the electric field intensity and polarization is changed locally, we might also expect a corresponding local variation of the preferential direction, leading e.g., to spatial oscillations of the shape (**Figure 7d**).

After the quasi-static investigation of a variety of wetting patterns we will now address dynamic responses of our surfaces that will play a role when spatio-temporally varying interference patterns are applied. The advantage of our experimental setup is that we will be able to track this dynamic process at various speeds, from a “stop motion” like fashion where the system (surface structure, surface + droplet) is allowed to relax for some preset time interval at each step, and also in a continuous mode, where the propagation of the interference pattern is assigned some velocity by adjusting the irradiation parameters. We note that the response of the structured surfaces upon exposure to light proceeds on at least two time scales. The instantaneous response from *trans* to *cis* isomerization is a change in surface energy, and only after seconds or even minutes the topography will adapt accordingly. When a liquid droplet is placed on such a substrate, it will respond to dynamical changes in the wettability resulting from these two different contributions (surface energy, texture). We will characterize in detail how, depending on the periodicity of the applied optical interference pattern to the size of the droplet, the latter responds when the speed of propagation is varied from small velocities (changing texture and surface energy together) to higher velocities where the droplet contact line is constantly kept from relaxing to its equilibrium shape, giving rise to new states of dynamic wetting. In particular this aspect shall be investigated in cooperation with H. Stark (TU Berlin), who will introduce the separation of time scales into his theoretical models.

WP3. Hierarchical structuring of pillar arrays (print mode).

In the previous work package we have described how to dynamically and reversibly change the hydrophobicity of a structured surface by making the structural elements (such as pillars) deform extensively. In this work package, we aim at investigating whether similar changes in wetting behavior can be produced without the deformation of a pillar as a whole but only at the contact area towards a droplet. We shall consider pillars of considerably larger dimensions (e.g., 5µm and more) the surface of which can be modified just in the same way as a continuous film. For instance, by applying interference patterns with periodicity smaller than the pillar dimension (e.g., 500nm) the pillars are expected to become rippled leading to similar local changes in surface energy as characterized in **WP 1** and **2** (**Figure 8a**). These changes would be superimposed on the hydrophobicity granted by the overall large scale shape of the pillars and their periodicity on the substrate. In other words, here we might be given a means to attain some fine tuning of hydrophobicity that might not be possible with the deformation approach. We emphasize that the hierarchical structuring is reversible as well. The topmost layer of a pillar can be rippled and

flattened many times in a dynamic manner. The grating vector additionally introduces some anisotropy, which could furthermore be exploited. In this respect we shall also test modified polymers containing liquid crystalline (LC) azobenzene side chains to test in how far anisotropy can be made to have a pronounced impact in the context of large pillars and posts. Note that in this case the topography of the pillar surface does not necessarily have to change (**Figure 8b**). Along with the study of nematic systems, we should account for an extensive scientific exchange and cooperation with the lab of Prof. Ralf Stannarius (Magdeburg) renowned for strong expertise in coupling azobenzenes to liquid crystals, and Prof. M. Oettel (Tübingen) showing strong interest in contributing with a computational description of the nematic aspects of our systems.

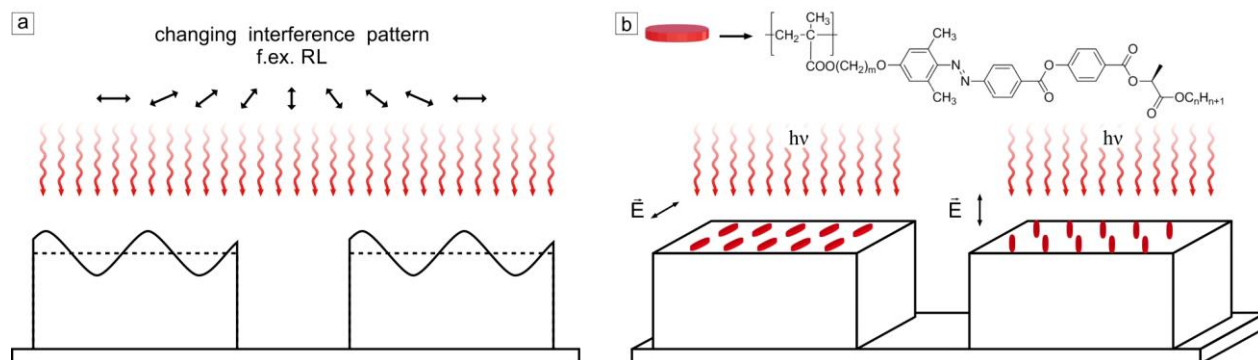


Figure 8. Scheme of how pillars can be structured locally. (a) Inscription of surface relief gratings and (b) inducing a certain nematic order of the azobenzene containing, liquid crystalline side chains. An example of a chemical structure of azobenzene containing liquid crystalline polymer is shown in b as well. Black arrow in (a) and (b) indicate distribution of electrical field vector.

WP4. Droplet manipulation by light induced dynamic control of liquid adhesion forces.

We should recall that along with each step in the previous WPs a comprehensive investigation of wetting properties has been acquired, including time scales for dynamic changes in topography and wettability. This is to be exploited in the current WP in order to manipulate adsorbed liquid droplets in a controlled way. The different dynamical structural changes investigated so far are in principle sufficient to define a certain set of basic operations that can be applied to adsorbed liquid droplets such as translocation and deformation, the combination of which may be used to realize defined processes of translocation, merging and mixing. The latter two processes are shown schematically in **Figure 9**, where two droplets adsorbed to neighboring lines of photosensitive polymer are brought in contact and forced to merge after varying the polarization distribution in a similar way as shown in **Figure 2** (the change in topography is indicated along the time axis and to be understood as a spatial direction). This could lead to applications such as reconfigurable microarrays. The challenge of devising an application is twofold. On the one hand we need to create local patterns of wettability by which a droplet's contact line can be caught, advanced and receded anisotropically to manipulate it without generating uncontrolled jumps. For instance, if we catch a droplet by a hydrophilic stripe generated by an interference pattern with periodicity matching the droplet size, how much further can the stripe be narrowed in order to stretch the liquid? What surface structure is the better choice for this purpose, a continuous photosensitive polymer film, an array of posts or lines? On the other hand, one may want to

address single droplets out of an ensemble of nearby ones without disturbing the latter. To achieve this, we shall combine the strategies of global irradiation (dynamically and periodically varying interference patterns) with local modifications such as application of a weak, focused laser spot, the shape of which may be designed.



Figure 9. Scheme of droplet merging and mixing on light induced dynamically changing polymer topography. The change in topography is indicated along the time axis and to be understood as a spatial direction. “ t ” indicates time.

Table 1. Project schedule.

Work package	Year 1	Year 2	Year 3
WP°1. Generation of structured arrays of photosensitive material and characterization of response under irradiation with different interference patterns.			
WP°2. Light induced dynamic fluctuations in arrays of structural elements (shape mode).			
WP°3. Hierarchical structuring of pillar arrays (print mode).			
WP°4. Droplet manipulation by light induced dynamic control of liquid adhesion forces.			

2.4 Data handling

Data acquired within this research project will be archived electronically (multiple backup) and can be accessed by the members of group at any time (read access). In our group, each co-worker is obliged to maintain an electronic lab journal. This is a data repository (Tortoise SVN), by which all documents relevant to the project (descriptions and experimental parameters,

spectra, tables, figures etc.) are stored on the desktop computer of each staff/project member. The repository is synchronized and backed up on a server. This will facilitate reconstructing the history of experimental conditions, the evolution of settings and parameter a.s.f. The server is located within the group of experimental physics, archived by a RAID-system, with daily backup on a server in the computer science center of the university. Staff members/researchers are repeatedly informed that only appropriately archived data can be part of scientific publications.

2.5 Other information

Not applicable

2.6 Explanation on the proposed investigations

Experiments involving humans, human materials or animals will be not carried out.

2.7 Information on scientific and financial involvement of international cooperation partners

No close or well-defined collaboration is intended with international cooperation partners.

2.8 Information on scientific cooperation within SPP2171

For our proposed work it is of great importance to have support from theory and computation. We plan to sustain extended collaborations with the group of Prof. Holger Stark. Prof. Stark intends to study the wetting behavior on photoswitchable surfaces. The scientific goals he puts forward shows strong overlap with ours, and cooperation in this case can be rather fruitful for both groups. Details of the planned collaboration are noted in WP2. The PhD student to be hired for our project will be expected to communicate frequently with the Stark lab. We do not request extra funding for the corresponding traveling due to the close proximity Potsdam-Berlin. Additionally we would like to cooperate with two other theoretical groups, the first one is Prof. R. Stannarius (Magdeburg) and Prof. M. Oettel from Tübingen University. These collaborations are explained in more details along with WP3. From both groups we expect insight into the nematic aspects of our photosensitive polymer films.

We also plan to collaborate with other experimental groups such as the lab of P. Huber (Hamburg) who is going to trigger adaptive wettability by applying electric fields; the group Prof. Böker/Dr. Reinicke (Fraunhofer IAP Potsdam) making use of mechanical stimuli, and the lab of Dr. Hussong and Dr. Guerevich (Bochum), using magnetic fields. Here we will continuously exchange results on efficiency and extent to which either method can lead changes in wettability in order to put each method into context.

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4. Requested modules/funds

4.1 Basic Module

4.1.1 Funding for Staff

The proposed project is challenging experimental work which requires a great dedication and care, thus justifying the application for one PhD position.

1 PhD student (NN) for 3 years **3/4 EG 13**

The PhD student should preferentially be a physicist or engineer, as he or she shall primarily be occupied with establishing the technical goals of the project, i.e. connecting the different experimental setups. All four experimental work packages will be carried out by this student.

The different types of azobenzene containing polymers will be synthesized in the group of Prof. Santer and can be provided to the student on demand.

4.1.2 Direct Project Costs

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

For this project in our laboratory consumables are needed per year (related to this project) as follows:

Optical Elements	10.000 €
Chemicals	9.000 €
Electronics and mechanical elements	9.000 €
AFM Tips	9.000 €
Sum for three years:	37.000 €

4.1.2.2 Travel Expenses

Travel expenses requested divide into two parts, the first one comprising solely SPP related costs such as workshops and participation of the student in one international conference. The second part relates to the regular load of conferences that is usually required for my PhD students bring their presentation skills to an appropriate level and to educate them for their further career in science.

Direct SPP related costs:

Two SPP workshops	1.100€
Advanced School	1.200€
PhD-candidate workshop	600€
International conference	1.200€
Total (SPP)	4.100€

Additional conferences	
3×National conferences (e.g. DPG)	1.500 €

2xInternational conferences (e.g. ACS, EPF and etc.) 3.000 €

Sum for three years 8.600 €

4.1.2.3 Visiting Researchers

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 publication costs of ca. **750€ / year**. These include the cover pages and color figures charges as well as online journal costs.

Sum for three years 2.250 €

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

5. Project requirements

5.1 Employment status information

Prof. Dr. Svetlana Santer has a W2-Professor position at the University of Potsdam.

5.2. First-time proposal data

Not applicable

5.3 Composition of the project group

- Prof. Dr. Svetlana Santer (W2 Prof.), head of the experimental physics group, Institute of Physics and Astronomy, University of Potsdam
- Dr. Jürgen Reiche is an expert for polymer thin film fabrication, X-Ray reflectometry and diffractometry
- Mrs. Stabenow as a technical assistant is responsible for the electron microscopy equipment. She will assist the PhD student in characterizing the fabricated samples.
- Dr. Nino Lomadze is a chemist and will synthesize required photosensitive polymers.

5.4 Cooperation with other researchers

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

None

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

1. Prof. O. Vinogradova (Theory), (RWTH, Aachen, Germany), light driven diffusioosmotic flow.
2. Prof. Jan Genzer (NCSU, USA) (Chemistry), research on polymer brushes
3. Dr. Olga Guskova (Theory), (Leibniz Institute of Polymer Research Dresden, Germany) photosensitive polymers.
4. Prof. El. Kramarenko (Theory), (Moscow State University, Russia), photosensitive microgels.

5.5 Scientific equipment

For conducting the proposed research we have unrestricted access to the instruments and facilities of the Institute for Physics and Astronomy. Technical facilities in detail:

- For advanced analysis and imaging, an Atomic Force Microscope (AFM) (NT-MDT) is available, capable of acquiring 3D-Images of suitably prepared samples. Various imaging modes may be employed: Contact Mode, Non-Contact Mode, Tapping Mode, Lateral Force, Force-Modulation and Phase-Detection, Kelvin-Mode.
- Second AFM (MI Pico) especially equipped and devoted to *in-situ* investigations where the sample is irradiated by UV-light and Veeco AFM for fast and routine imaging applications.
- Standard equipment for optical microscopy
- Facilities for ellipsometry
- UV- and IR-Spectrometer
- X-Ray Diffractometer and Reflectometer
- Various facilities for soft matter research, e.g. Langmuir-trough, Spin-Coater, Dip-Coater, Sputter equipment and facility, plasma etching facility and equipment, equipment for carrying out photolithography etc. for fabrication and modification of thin films and surfaces
- SNOM and SEM, shared with the laboratory of Prof. Neher (also Institute for Physics and Astronomy)
- Chemical laboratories and equipment for all routine tasks
- Laser laboratory equipped with a facility for carrying out interference nano-lithography and surface Plasmon interference nano-lithography.

5.6. Project-relevant interests in commercial enterprises

The applicants are not the owners of a commercial enterprise and are not stakeholders in one.

6. Additional information

For this research proposal, we did not apply for funding at any other agency or organization. Should we decide to do so, we will notify the Deutsche Forschungsgemeinschaft immediately.