

Proposal for SPP 2171: Dynamic wetting of flexible, adaptive and switchable substrates**Prof. Dr. Björn Braunschweig**

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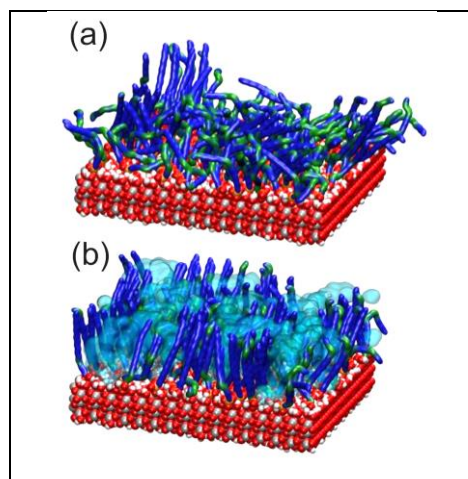
Structure-Property Relations and Wetting Dynamics of Organic Thin Films with Photo-Switches**Project Description**

Figure 1 Snapshots from MD simulations of octadecane phosphonic acid SAMs on α - Al_2O_3 with a coverage of 2.57 molecules/ nm^2 . (a) SAM in vacuum/inert gas (b) in 2-propanol. Blue colored sections of the alkyl chains indicate trans-configurations while gauche-defects are highlighted. A in green color. 2-propanol is shown as transparent clouds. Adapted from our previous work¹ together with Zahn and co-workers – experiments are in Fig. 2 and discussed below.

1 State of the art and preliminary work

Smart surfaces that can reversibly change their wetting properties are of great interest for applications such as self-cleaning surfaces, microfluidics or tunable lenses just to mention a few. However, even for passive surfaces that do not change their molecular properties when broad in contact with a liquid, a quantitative description the wetting dynamics is still a challenging issue. That is in particularly true when changes on the molecular scale due to adaptation of the substrate in different chemical environments or due to photo-switching of the substrate need to be taken into account as well. Previously, we have shown that even very simple soft self-assembled monolayers that are composed of long alkyl chains (e.g. C_{12} or C_{18}), show a different molecular structure when they are wetted or dewetted from a polar solvent (Figs. 1 and 2). For that reason, we believe that an understanding of the wetting dynamics of photo-switchable substrates requires molecular level information on the substrate dynamics and structure changes under different light conditions as well as different chemical environments. In order to resolve the latter we propose to perform characterizations and analysis on different length scales, where both molecular structure changes as well as mesoscopic and macroscopic properties are addressed and correlated.

In this project, we want to concentrate on photo-switchable substrates because they allow localizing the changes in surface properties and energies by a suitable confinement of the external light stimulus in time and space. For instance, the light-induced trans/cis isomerization of photo-responsive moieties such as azo derivatives within a self-assembled monolayers (SAMs), Langmuir-Blodgett films, polymer films etc. can be used to change the interfacial molecular structure, interface energies and thus the wetting properties substantially.^{2–6} In the past, the change of wetting properties was studied for photo-responsive substrates often using static^{2,4} contact angle measurements and in some cases also by measuring the dynamic⁷ change in contact angle (CA) after irradiation with different wavelengths (e.g. UV vs. visible light). Depending on the system under investigation the changes e.g. in the contact angle can be varied to a large extend. For instance, for dye-sensitized TiO_2 surfaces Kwon et al.⁷ showed that the contact angle was reversibly changed by $\sim 40^\circ$ when the light irradiation was changed. This is different for thin films with polymers having an azobenzene group and fluorinated residues. Here, R  he and co-workers²

have shown that for flat substrates the differences in CA with light irradiation are with $<20^\circ$ comparatively small, but could be dramatically enhanced to $>120^\circ$ for nanorough silicon black substrates. While the substrate structure and morphology can be an important asset for a surface to change its wetting properties under light irradiation, also the structure of the switchable organic film can be important. This has been demonstrated for self-assembled monolayers of azobenzene alkane thiolates on extended Au surfaces and Au nanoparticles. On flat surfaces, molecules in a SAM can be closed-packed when the growth and formation of the SAM is adjusted accordingly. However, close packing of molecules inside the layer can also have dramatic consequences for the ability of the layer to change its structure and thus to change its interface energy under light irradiation. Weinelt and co-workers⁵ have studied the latter issue systematically and found for densely-packed layers with azobenzene moieties virtually no response to light in their photo-switching experiments while 'diluted' SAMs of mixed alkane thiol and azobenzene thiol layers showed substantial switchability. This is consistent with an earlier report by Valley et al.⁸, who showed with sum-frequency generation (SFG) spectroscopy (see Panel 1) that 100% azobenzene SAMs do not exhibit photo isomerization due to tight packing, but reversible switching (>10 cycles) in mixed SAMs with only 34% and 50% of alkane thiol spacers was possible. Similar effects of the composition of mixed SAMs as well as substrate roughness on the responsiveness to pH, was shown by Yu et al.⁹

In case of light-responsive layers, steric hindrance is obviously likely to impair the layer's ability to change its structure with light irradiation and is yet another issue that has to be taken into account for dynamic wetting on photo-responsive substrates. In addition to the latter intrinsic properties of a photo-switchable layers, also extrinsic properties such as the presence of a gas or a liquid layer can lead to a substantial change in the switching ability or switching kinetics. This has been shown by Moldt et al.⁶ for azobenzene alkane thiol SAMs in vacuum (or dry N_2) compared to identical SAMs in ambient air. Here, the thermal relaxation from cis to trans conformations after irradiation with UV light and sample storage under dark conditions was in the order of minutes in vacuum/dry N_2 but extended to more than one day in ambient air. Moldt et al. propose that the presence of water molecules stabilized the cis conformation and yielded slower thermal relaxation. Because of slower thermal relaxation under ambient air conditions also the yield for photo isomerization under UV light was significantly higher under ambient conditions ($\sim 95\%$ cis) as compared to the situation in vacuum/ dry N_2 (50-74 % cis).

In our own work, we have shown previously that even simple self-assembled monolayers (SAMs) such as alkyl phosphonic acid SAMs on smooth (root mean square roughness <1 nm) α - Al_2O_3 single crystals adapt to the presence of polar solvents such as water and 2-propanol.¹

In Figure 2 we show some experimental evidence of the latter. Before, we can discuss the close analysis of the SFG spectra in Fig. 2, we need to make some general remarks on the analysis of C-H stretching bands which are in the present case extremely informative. That is because SFG is a coherent and inherently surface-specific technique (see Panel 1 for more information), and the amplitude of a vibrational band does not only depend on the molecules' surface coverage, but also on the molecular order of the surface layer under investigation. For examples of the latter from our own work, we refer to the project relevant publications section.

In case, the molecules in an alkyl SAM e.g. with octadecyl phosphonic acid (ODPA) moieties are in an all-trans conformation, symmetric methylene stretching vibrations at 2850 cm^{-1} do not give rise to significant SFG intensities. This in fact originates from the local inversion symmetry of methylene groups when all molecules are in an all trans state. The local inversion symmetry causes cancellation of all methylene signals because their orientational average is zero.

However, as soon as gauche conformation are present in the system, the overall SFG intensity decreases because the net orientation of the molecular hyper-polarizabilities are lower. For that reason, the SFG intensity and the ratio of SFG amplitudes from methylene and methyl (the terminal group of an alkyl SAM) are indicators for the molecular order inside an alkyl SAM. A decrease in molecular order will decrease the overall intensity and increase the CH_2/CH_3 intensity ratio.

Having discussed the latter dependencies of the SFG intensity, it becomes clear from a close inspection of Fig 2a-c that dewetting in the presence non-zero surfactant concentrations in the bulk solution, significantly improves the molecular order of a SAM. This observation in our experiments^{1,10} has been explained by a quasi-Langmuir-Blodgett transfer at the three-phase contact

line and is corroborated by MD simulations¹ which were performed by our previous collaborators (Prof. Dr. Dirk Zahn and Dr. Hanno Dietrich, FAU Erlangen Nürnberg).

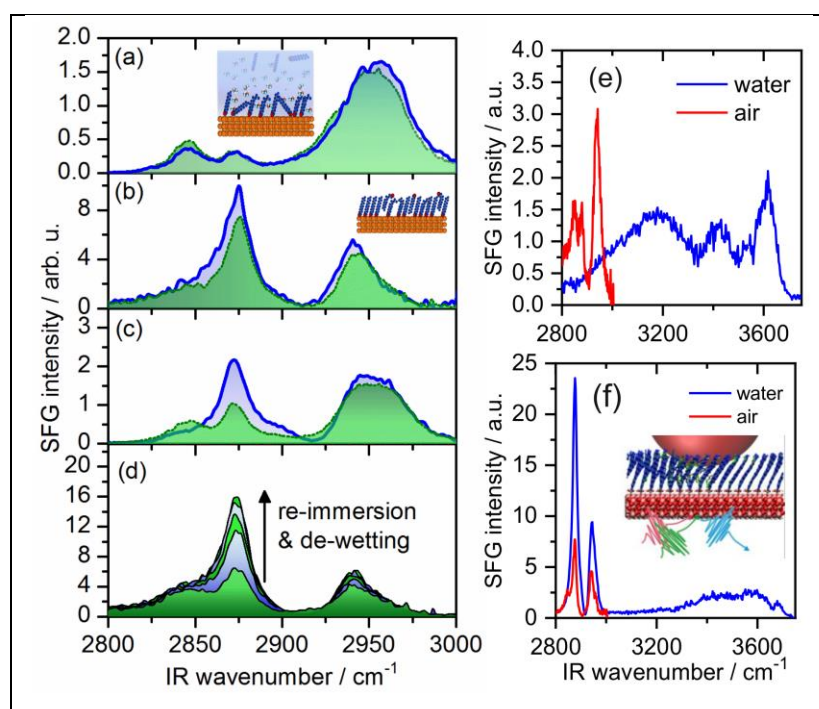


Figure 2 (a-c) *In situ* SFG spectra and comparison of de-wetting effects for 2 mM octadecane phosphonic acid (ODPA) solution (blue solid lines) and for a dilution with $C_{ODPA} < 0.02$ mM (green dotted lines) in contact with α -Al₂O₃.¹ (a) shows the SFG spectra after 0.5 h SAM growth in concentrated (blue lines) solution, while green lines indicate the SFG spectrum after 30 min growth time and subsequent dilution. (b) SFG spectra after de-wetting the sample in a flow of N₂ and in (c) after re-immersion of the de-wetted layers in blank 2-propanol are presented. (d) SFG spectra of ODPA deposited within 0.5 h for five de-wetting and immersion cycles. (e) and (f) SFG spectra of octyl (C₈) as well as octadecane (C₁₈) phosphonic acids, respectively, in contact with air and water. **(a-g) adapted from our previous work by Meltzer et al.¹; (h) and (i) unpublished data.**

Using MD simulations and SFG spectroscopy, we have also investigated the structure of alkyl SAMs in different environments (gas/vacuum vs. polar solvent). Snapshots from these simulations are presented in Figs. 1, where we compare ODPA SAMs with different coverages. In air, the low density SAM with 2.57 molecules/nm² shows a high density of gauche conformations, which are indicated by alkyl groups in green color while chains in trans conformation are shown in blue color. The SAM with low coverage is obviously disordered in air (Fig. 1a). Adding a 3-nm-thick layer of 2-propanol results in an increase in conformational order within a relaxation time of 10 to 20 ns¹ (Fig. 1b). This phenomenon is accompanied by solvent molecules penetrating the loosely packed layer and reducing the free space available to the surface-adsorbed ODPA molecules. In fact, the polar solvent leads to a segregation of the ODPA alkyl chains in such a way that small domains of improved packing are formed.

Consequently, an ODPA SAM with low density comprising a

comparatively high concentration of gauche defects in vacuum/gas becomes more ordered when the SAM is wetted with 2-propanol – the SAM adapts to different environments.

In case of a close-packed SAM with 3.8 molecules/nm² this adaptive behavior is not observed (not shown in Fig. 1), but such surface coverages are hardly obtainable in experiments where realistic surface coverages will be between the discussed extremes (2.57 and 3.8 molecules/nm²).^{1,10,11} In Figs. 2e-f we compare the changes upon wetting (air vs. H₂O) of ODPA (C₁₈) and an octyl phosphonic acid (C₈) SAM on Al₂O₃ substrates. Note that the molecular order of SAMs with shorter alkyl chains is per se lower as we have shown previously.¹² For short chains, wetting with water leads to complete destruction of existing molecular order and to complete loss in C-H signals compared to the situation when the C₈-PA SAM is in contact with air. This is different for the SAM with longer alkyl chains, where in fact a further improvement of the molecular order is observed. The latter can be concluded from the spectra in Fig. 2f, because the ratio of CH₂/CH₃ intensities decreases while the overall SFG intensity is increased. This observation is consistent with earlier MD simulations of C₁₈-PA SAMs in contact with 2-propanol (see above discussion and Fig. 1). However, the changes of the C₈-PA SAM upon wetting with water is yet not fully understood.

P1 Principles of Sum-Frequency Generation (SFG)

In dipole approximation the polarization induced by an external electric field can be written as series of linear and nonlinear contributions: $P_{\alpha}(\vec{r}, \omega) = \varepsilon_0 \sum_{\beta} \chi_{\alpha\beta}^{(1)} E_{\beta} + \varepsilon_0 \sum_{\beta\gamma} \chi_{\alpha\beta\gamma}^{(2)} E_{\beta} E_{\gamma} + \dots$

Here, $\chi_{\alpha\beta}^{(1)}$ and $\chi_{\alpha\beta\gamma}^{(2)}$ denote the linear and second-order electric susceptibility, respectively. In materials with centrosymmetry $\chi_{\alpha\beta\gamma}^{(2)}$ vanishes in the bulk due to symmetry reasons. Surfaces and interfaces, however, are a break in bulk symmetry and thus give rise to dipole allowed non-zero contributions. In sum-frequency generation (SFG) and second-harmonic generation (SHG) the effective susceptibility $\chi^{(2)}$ of an interface as a series of non-resonant and resonant contributions described by Lorentzian functions where the impinging frequency resonantly excites vibrational modes or electronic transitions of molecules at interfaces.

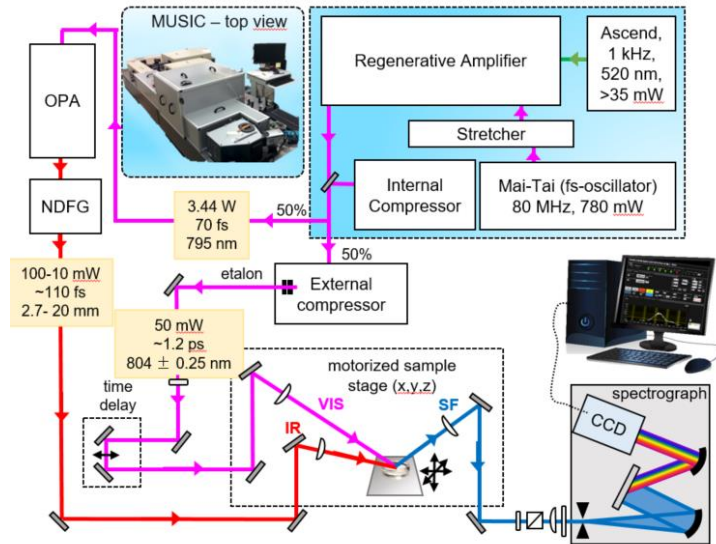


Figure P1a: Schematic drawings of our MUSIC spectro-meter (Münster Ultra-Fast Spectrometer for Interface Chemistry) that uses vibrational sum-frequency generation (SFG). In SFG spectroscopy tunable broadband IR pulses and time-asymmetric narrowband pulses at 800 nm are used.

In vibrational SFG, photons with IR frequencies ω_{IR} and photons with a frequency in the visible region ω_{vis} are mixed to generate the sum frequency $\omega_{SF} = \omega_{IR} + \omega_{vis}$ (see Fig. P1a), while in SHG two photons are mixed to generate a third photon with the second-harmonic frequency. In both cases, the amplitude A_q each contribution is a function of net molecular orientations at an interface, while the amplitude of a species is determined by the molecular hyper-polarizability β_q , the interfacial number density N , and the orientation distribution of the contributing molecules $f(\Omega)$. A_q needs to be expressed by an integral over all possible molecular orientations at the interface

(P1) $A_q = N \int f(\Omega) \beta_q(\Omega) d\Omega$.

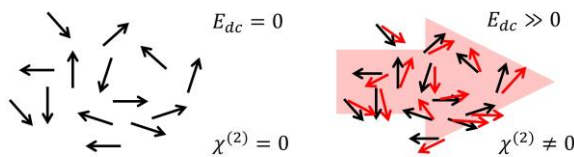


Figure P1b: Electric field polar ordering at field at field strengths $>10^8$ V/m.

Therefore, random orientations of molecules or molecular arrangements with centrosymmetric structures like in bulk liquids or gases will lead in dipole approximation to negligible intensities because the integral in eqn. (1) vanishes in this case. A perfectly ordered adsorption layer with well-aligned molecules results, however, into the highest amplitude and SFG intensity. In addition, the presence of an electric field at the interface can cause additional contributions that are directly depending on the electric field and on polar ordering of molecules.

$$P_{2\omega}^{(2)} \propto \chi^{(2)} : E_{\omega_1} E_{\omega_2} + \chi_{dc}^{(2)} : E_{\omega_1} E_{\omega_2} + \chi^{(3)} : E_{\omega_1} E_{\omega_2} \int_0^\infty E^{dc}(z) e^{-\Delta k \cdot z} dz$$

Using nonlinear optical spectroscopy it is possible to determine molecular compositions, surface charging and molecular orientations at buried interfaces such as solid-liquid interfaces. However, an unambiguous assignment requires often complementary methods.^{13,14}

In addition to the discussed changes in C-H stretching bands, the interfacial water structure is also different when comparing Fig. 1e with 1f. That is because the broad O-H bands at 3200 (more ice like water^{15,16}) and 3450 cm⁻¹ (more liquid like water^{15,16}) due O-H stretching vibrations of hydrogen bonded interfacial water molecules as well as the free O-H stretching band^{15–17} at ~3700 cm⁻¹ change between C₈ and C₁₈ SAMs. Both scenarios bring strong evidence to our conclusion that the wetting behavior of soft substrates such as self-assembled monolayers is coupled to structure changes of the interfacial layers.

Having discussed the above reports on the adaptive behavior of soft layers as well as the switching ability of photo-responsive layers we can establish already four key challenges that need to be addressed for dynamic wetting transitions at photo-switchable substrates:

- **Even in the absence of additional surfactants that can additionally adsorb to the interfaces in the system under investigation, the liquid phase from a wetting film or a liquid drop can induce structure changes of the soft (photo-responsive) self-assembled monolayer.**
- **In order, to address dynamic changes of the latter during wetting transitions, both equilibrium and non-equilibrium (switching kinetics etc.) information on relevant interfacial molecular structures are needed.**
- **Both the molecular structure in contact with a liquid and a gas is different; wetting dynamics will inevitably lead to hysteresis.**
- **Because the ability to respond to light stimuli is strongly linked to the packing density with photo-responsive moieties (steric hindrance needs to be avoided) structure changes during wetting will also cause changes in the responsiveness of the interfacial layer to light stimuli.**

Recently Butt et al.¹⁸ have proposed a model, which quantitatively links the contact angle hysteresis and the dynamic contact angle to adaptation processes of ‘soft’ surfaces. In their work, the authors do not address photo-switchable soft substrates, but address cases where the samples molecular structure is disturbed by the presence of a liquid or its vapor. Taking the above discussion into account photo-switchable layers can change their properties as a function of light irradiation but do also adapt to the presence of liquid. They therefore fall into both categories proposed for **SPP 2171**. Examples for adaptive substrates mentioned by Butt et al.¹⁸, are the behavior of polymer reconstructions, diffusion and swelling of polymers in contact with liquids but also self-assembled monolayers.^{9,18} One important parameter in the model is the assumption of first order kinetics with the so-called relaxation time τ corresponding to the time needed for the solid-liquid interface to adapt. τ can range from a few ns (molecular scale ordering of liquids), formation of an electric double layer (<1 μ s) , diffusion and adsorption of (low molecular weight) surfactants (<1 ms to several minutes).

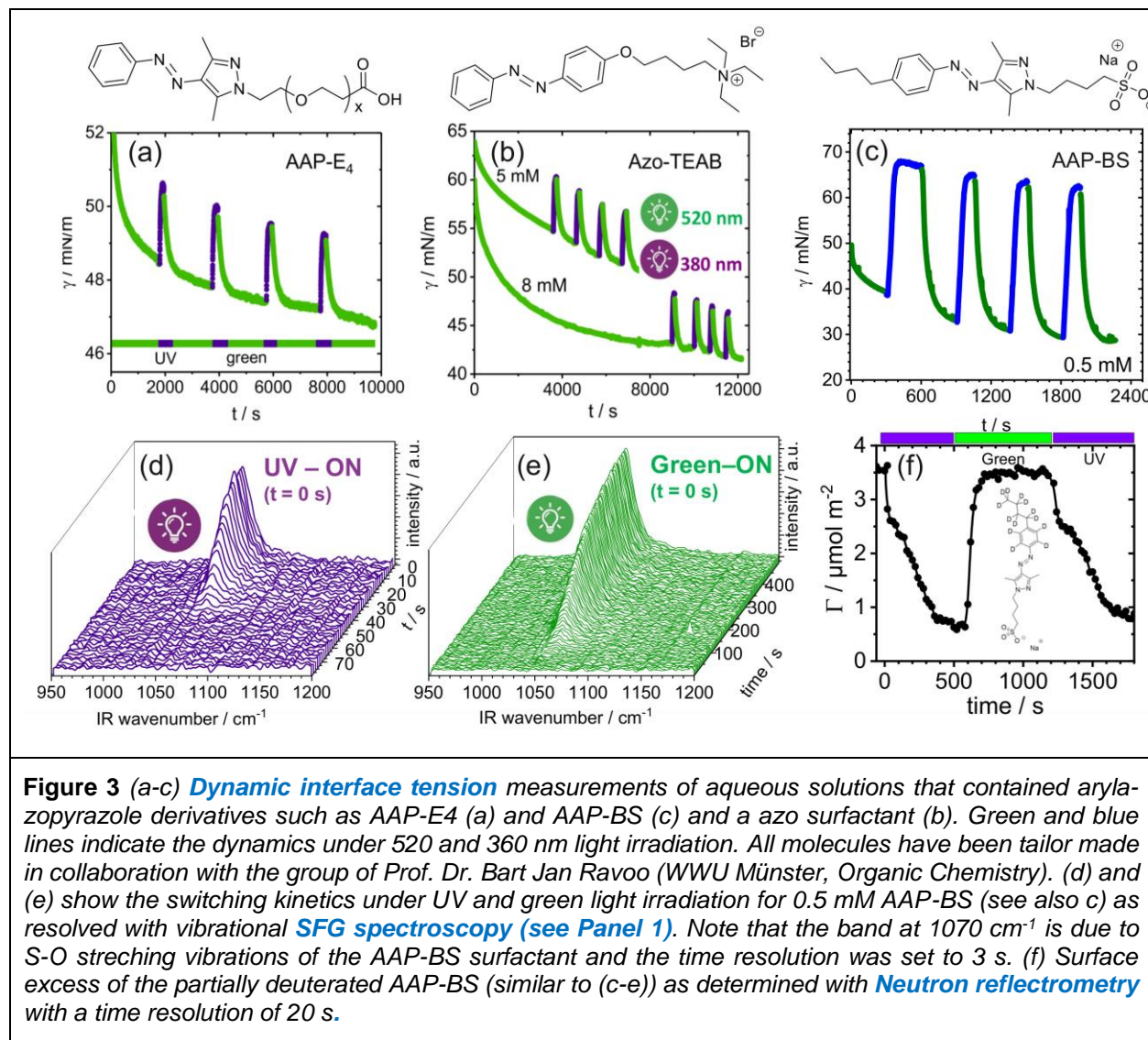
Butt et al. also state, “[...] We did not find quantitative experimental relaxation times with respect to reconstruction of organic monolayers or the replacement of contaminants or adsorption layers [...]”.

Since SFG spectroscopy (Panel 1) is a powerful tool, which can provide such information, we strongly believe that the use of our method can be of special interest for several other projects within SPP 2171 that deal with adaptive and/or switchable substrates.

On the choice of substrates and molecules

As already discussed above, previous works have focused on the use of azo polymers and azo surfactants which were deposited on a solid surface.^{2–6,8} Azobenzenes are particularly interesting, because they can reversibly switch between trans to cis configurations without any bond breaking. This change in the molecular configuration leads to a significant change in the electronic as well as the steric structure of the surfactant and thus allows for switching its surface activity (as a surfactant) but also the interface tension (when permanently adsorbed to a solid surface). Consequently, also the free energy landscape of an interface can be modified by light irradiation. As

a result, to light-induced changes of the wetting behavior are possible. Although there exist extensive work of azobenzene derivatives and their wetting behavior under equilibrium conditions. Non-equilibrium conditions and wetting dynamics as a function of time and light irradiation have been studied to a far less extend. Even at the far simpler gas-liquid interfaces that were decorated with photo-switchable amphiphiles, dynamic changes has been addressed to a much less extend and are still fairly understood on a molecular level.



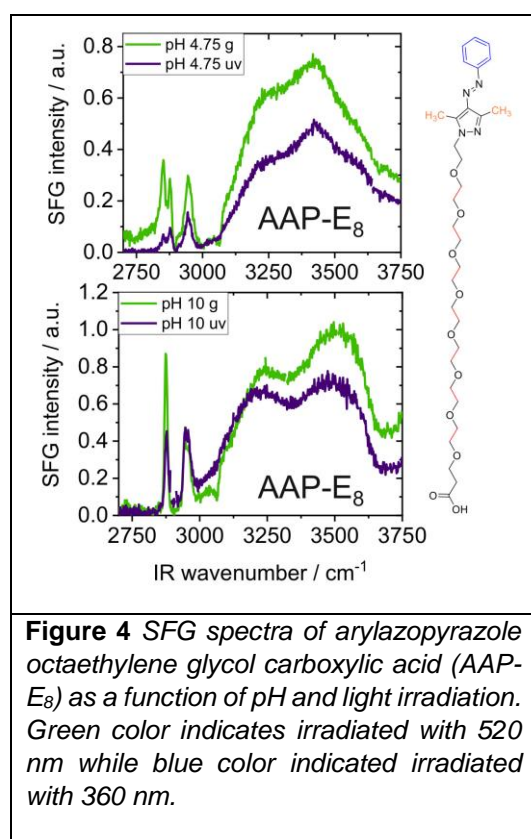
Different from many pervious works on photo-switchable interfaces, where mostly azo derivatives have been used, we follow a different approach in our work,¹⁹ and make use of a new class of photo-switchable molecules namely arylazopyrazole (AAP) derivatives. Our collaborators - Prof. Dr. Bart Jan Ravoo and his group - have pioneered the development and application of AAPs for various purposes such as photo-switchable amphiphiles for smart air-water interfaces, which can respond to light and can drive structure-property relations in aqueous foam.

Arylazopyrazoles are superior analogues of azobenzenes with much more favorable thermal half-life times compared to most azobenzenes and a smaller spectral overlap of the trans and cis isomers which results into a more favorable photostationary state with >95 % switching in both directions.^{20–22} Since APPs are new class of photo-switches, they have not been studied so far in terms of (dynamic) wetting behavior.

In Fig. 3, we present examples of AAP amphiphiles which have been tailor made in the group of Prof. Dr. Bart Jan and his co-workers (e.g. Dr. Lucas Stricker, AAP-E₄) as well as in our own group (by Christian Honnigfort (AAP-BS) and Marco Schnurbus (Azo-TEAB)). In Fig. 3, we

demonstrate that AAPs show unprecedented reversibility of their behavior at air-water interfaces, while we can use moderately low concentrations, which are smaller than the surfactants critical micelle concentration.

From Fig. 3, it becomes clear that AAPs can reversibly modulate the water's interface tension and can lead in case of AAP-BS to even dramatic changes in the interface tension of >25 mN/m. AAP- E_4 and Azo-TEAB surfactants also show a high reversibility of their interfacial behavior, the modulation of the interface tension is, however, moderately small. At this point, we can only speculate on the origin of the observed differences, but this issue is part of ongoing investigations of the latter surfactant. While tensiometry already gives a good overview on the surfactants switching behavior at the interface in terms of switchability and reversibility, the molecular mechanism is less clear. In order to resolve the latter, we have performed additional experiments with SFG spectroscopy and specular Neutron reflectometry (NR). NR was done at the FIGARO experiment situated at the Institute Laue Langevin (Bart Jan Ravoo (WWU Münster and Richard Campbell (U Manchester) as co-proposer). For our discussion, we want to focus only on AAP-BS and AAP- E_8 (Fig. 4) surfactant as the others show similar but less pronounced changes in their interfacial behavior as a function of light irradiation. For additional information on AAP- E_4 surfactants we refer to our published results (Schnurbus et al.¹⁹).

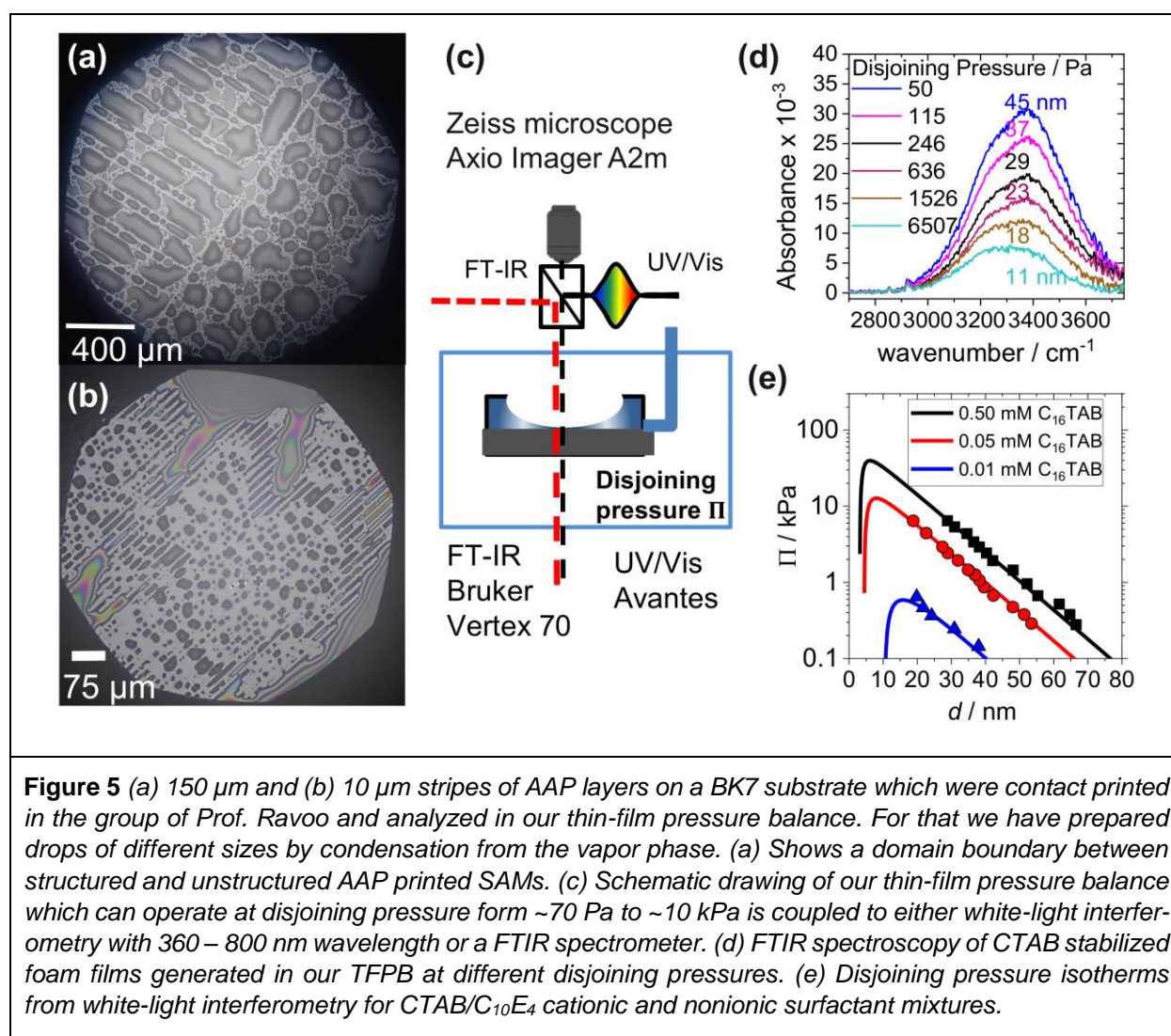


$\mu\text{mol}/\text{m}^2$ (Fig. 3f) within less than 120 s (UV to green) and 10 min (green to UV). This unprecedented result was unexpected because a structural change from trans to cis conformations does not necessarily result in such a major change in surface activity.

In Figure 4, we present SFG spectra of air-water interfaces that are modified by AAP- E_8 amphiphiles, which demonstrate that substantial changes occur when the pH is changed. An increase in pH leads to additional charging of the interface due to (de)protonation of the acid groups of interfacial moieties. Surface charging causes the increase in O-H intensity because of additional polarization and polar ordering of interfacial water molecules (see general details on that in Panel 1). Particularly interesting are also the change in C-H bands. Methylene bands (2850 cm^{-1}) are observed at low pH while at high pH, the SFG intensity of the latter is negligible and the spectra are dominated by the methyl stretching (2880 cm^{-1}) vibrations. UV irradiation causes an overall decrease in SFG intensity at both pH, which is for this interface related to a reduction of the surface excess according to our NR data (not shown). However, at low pH we do also observe

In our NR experiments, we have demonstrated for the first time (allocated beam time at ILL was 11.-14.09.18) dramatic changes in the surface excess of butyl arylazopyrazole sulfonate surfactants (Fig. 3f, structure data are currently analyzed). The NR results with deuterated AAPs are corroborated by our SFG experiments. In Fig. 3d and e we show time-resolved SFG spectra of the S-O stretching vibration and under UV and green light irradiation. Initially the surface was brought in equilibrium under green light irradiation (520 nm), which can take up to several minutes (Fig. 3c). Fig. 3d shows the changes after the green light was switched off and the UV light was simultaneously switched on. Here, a drastic decrease in S-O intensity was observed on a very short time scale of less than 120 s. Fig. 3e shows the reversed process - UV off and green on -, where the S-O intensity recovered but on a much longer time scale of roughly 5 min. In fact, this is consistent with our NR of deuterated (Fig. 3f) and non deuterated surfactants (not shown), where we were able to resolve the change the surface excess on a sub-minute time scale and at relatively moderate bulk concentrations of 0.25 mM. The figure shows that the surface excess changes from $\sim 3.5\text{ }\mu\text{mol}/\text{m}^2$ for the deuterated molecule to very low values of <0.7

a change in the CH_2/CH_3 intensity ratio. Because only gauche conformations can give rise to CH_2 signals of AAP- E_8 adlayers, the change in the CH_2/CH_3 intensity ratio must be related to an increased molecular order of the ethylene glycol chains (reduction of gauche conformations at the interface). From a close inspection of the SFG spectra in Fig. 4, we can also observe that the weak aromatic C-H stretching band at 3060 cm^{-1} , which shows up as a dispersive feature on the broad O-H contribution, is reduced to negligible intensities under UV light irradiation. This reduction in intensity is again due to a reduction in surface excess, however, according to the changes in CH_3 intensity a weaker change would have been expected. The more extensive reduction in intensity is attributable to an orientational change of the AAP from a more vertical (under green light) to a more parallel orientation where the net dipole moment of the aromatic C-H modes in direction to the surface normal is zero and thus leads to negligible SFG signals.



Additional methods we plan to apply within in this project.

In order to address not only the thickness but also the composition of wetting films we have extended the abilities of a classical thin-film pressure balance (TFPB).^{23,24} Particularly, we can now couple a TFPB to a FTIR spectrometer, which allows to record IR absorbance spectra of thin-liquid films (Fig. 5). From these spectra we can determine the film thickness as function of disjoining pressure without assumption for the thickness of the interfacial layers. The determination of the water core thickness in thin films directly from the absorbance that arises from e.g. O-H stretching modes is of great importance because it does not require a priori assumptions on the thickness of the adsorbate layer which is actually needed when applying white-light interferometry (which is the existing approach to thin-liquid films so far). For that reason, our new experimental

approach can be also used for rather complicated wetting films on photo-switchable surface layers without changing the layer properties. In fact, white-light interferometry at wetting films on photo-switchable substrates will be challenging because the method will cause unwanted structure changes (cis/trans photo-isomerization) during the measurement already. Using mid-IR light for film thickness determination, will avoid such experimental issues. In Fig. 5d, we present an example where thin films with thicknesses between 11 and 45 nm have been successfully measured in our setup. From an analysis of Fig. 5d, it becomes also clear that our signal-to-noise ratio is also sufficient to measure wetting films much smaller than 10 nm. In Fig. 5e, we show disjoining pressure isotherm from white-light interferometry of foam films with different surfactant mixtures, which demonstrates that we are able to measure the disjoining pressure of thin liquid films in our new developed setup. In this project, we want to our setup to thin wetting films of extended photo-switchable substrates, but also to structured substrates. In Fig. 5 we show as an example how the mesoscopic and macroscopic wetting properties can be addressed on structured substrates using optical microscopy. In Fig. 5a and b we recorded micrographs of structured substrates which have been wetted by drops of different size. Although the wetting properties of structured surfaces have been extensively studied, little information on the wetting dynamics of structured and photo-switchable substrates exists so far. As we will explain in more detail in the work program, one objective of our proposed project is study the latter using well-defined contact printed photo-switchable SAMs.

1.1 Project-related publications

- [1] M. Schnurbus, L. Stricker, B.J. Ravoo, **B. Braunschweig**, *Smart Air-Water Interfaces with Arylazopyrazole Surfactants and Their Role in Photoresponsive Aqueous Foam*; Langmuir 34, 6028-6035 (2018)
- [2] C. Meltzer, H. Yu, W. Peukert, **B. Braunschweig**, *Molecular structure of octadecylphosphonic acids during their self-assembly on α -Al₂O₃(0001)*, Phys. Chem. Chem. Phys. 20, 19382-19389 (2018) (Part of **2018 PCCP Themed Hot Articles**)
- [3] J. Lützenkirchen, G. Franks, M. Plaschke, R. Zimmermann, F. Heberling, A. Abdelmonem, G. Darbha, D. Schild, A. Filby, P. Eng, J.G. Catalano, J. Rosenqvist, T. Aytug, T. Preoča, D. Zhang, Y. Gan, **B. Braunschweig**; *The surface chemistry of sapphire-c: A literature review and a study on various factors influencing its IEP*, Adv. Coll. Int. Sci. 251, 1-25 (2018)
- [4] A. Pathak, A. Bora, **B. Braunschweig**, C. Meltzer, H. Yan, P. Lemmens, W. Daum, J. Schwartz and M. Tornow, *Nanocylindrical confinement imparts highest structural order in molecular self-assembly of organophosphonates on aluminum oxide*, Nanoscale 9, 6291-6295 (2017)
- [5] M. A. Frank, C. Meltzer, **B. Braunschweig**, W. Peukert, A. R. Boccaccini, S. Virtanen; *Functionalization of steel surfaces with organic acids: influence on wetting and corrosion behavior*, Appl. Surf. Sci. 404, 326 (2017)
- [6] J. Paul, C. Meltzer, **B. Braunschweig**, and W. Peukert; *Lubrication of Individual Microcontacts by a Self-Assembled Alkyl Phosphonic Acid Monolayer on α -Al₂O₃(0001)*, Langmuir, 32, 8298 – 8306 (2016)
- [7] C. Meltzer, H. Dietrich, D. Zahn, W. Peukert, and **B. Braunschweig** *Self-Assembled Monolayers Get Their Final Finish via a Quasi-Langmuir-Blodgett Transfer*, Langmuir, 31, 4678 (2015)
- [8] C. Meltzer, J. Paul, H. Dietrich, C.M. Jäger, D. Zahn, T. Clark, **B. Braunschweig** and W. Peukert; *Indentation and Self-Healing Mechanisms of a Self-Assembled Monolayer - A Combined Experimental and Modeling Study*; J. Am. Chem. Soc., 136, 10718 (2014)

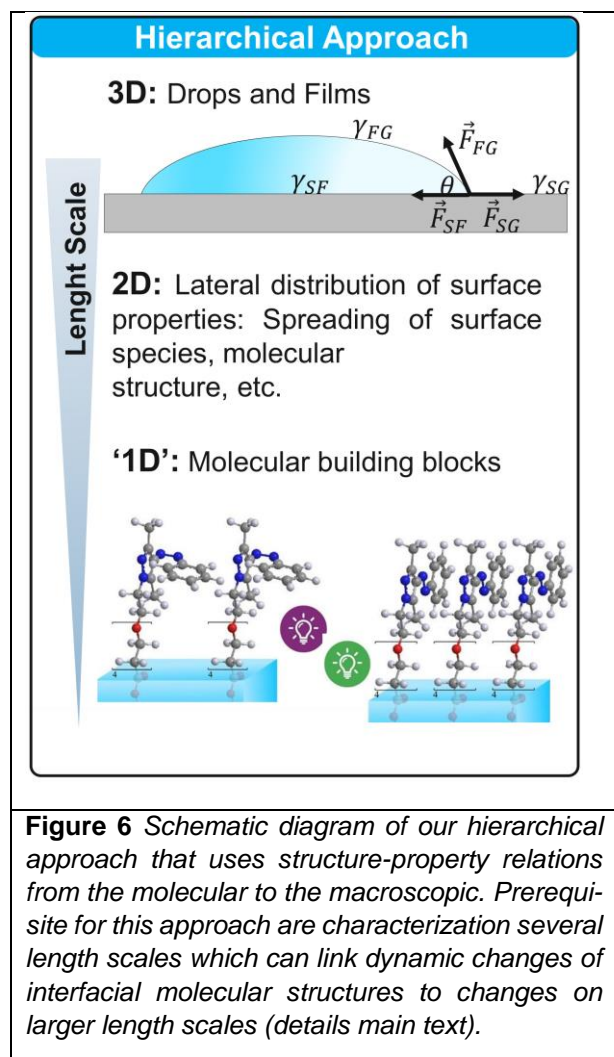
2 Objectives and work program

2.1 Anticipated total duration of the project

36 months

2.2 Objectives

In this project, we want to study solid surfaces that have been modified by adsorption layers with arylazopyrazole photo-switchable moieties and address the dynamic changes in wetting properties and molecular structure after reversible cis/trans photo isomerization.



Although the wetting properties of particularly azo derivatives have been addressed before, detailed information on the wetting dynamics of photo-switchable substrates as well as on a new class of photo-switchable molecules (arylazopyrazole, AAP) are so far not available.

Investigations of the wetting dynamics of photo-switchable substrates require information on several length scales. That is because, the molecular structure changes upon light irradiation determine the kinetics at the interface. Furthermore, the latter changes at the molecular scale drive behavior on micro and macro length scales e.g. advancing or receding contact angles. For that reason, we believe that structure-property relations from the interfacial to the macroscopic level exist and can be used to understand the wetting dynamics of a switchable substrate.

Consequently, we propose a hierarchical approach as shown in Fig. 6. In this approach, AAP building blocks are tailor made from organic synthesis and their assembly is controlled and structured at a solid surface by molecular self-assembly. On the interfacial level, we will perform characterizations with SFG spectroscopy (Panel 1) in order to get molecular structure information of AAP layers in and outside equilibrium conditions. In addition, we will perform mesoscopic and (thin wetting films, pre-wetting layers) and macroscopic (dynamic contact angles) characterizations. In the state-of-the-art and previous

work section, we have concluded that even very simple molecular layers on solid surfaces adapt to different chemical environments e.g. a polar liquid or an inert gas. This 'adaptive' behavior is mainly driven by structure changes that reduce the free energy of the relevant interfaces. An understanding of the wetting dynamics of photo-switchable SAMs on a solid support therefore requires knowledge of both structure changes of the photo-switchable SAM when brought in contact with a liquid and a gas phase, as well as the dynamic structure change caused by cis/trans photo-isomerization when the layer is irradiated by UV or visible light. We therefore propose the following major questions, which need to be studied in our project:

- 1) What is the structure of a photo switchable layers under equilibrium conditions and in different chemical environments (liquid/vs gas). What are possible relaxation dynamics/kinetics after (de)wetting?
- 2) What are the dynamic changes in interfacial molecular structure upon cis/trans photo-isomerization? What are the switching kinetics? For the latter, information on relevant interfacial molecular structures is needed.
- 3) How do 1) and 2) effect the wetting dynamics on larger length scales? (advancing/receding contact angles, pre-wetting layers, ...)

Our approach requires molecular-level characterizations of the solid-liquid, liquid-gas and solid-gas surfaces as well as characterizations on larger length scales. For the molecular level, we apply vibrational sum-frequency generation (SFG) which is a powerful nonlinear optical tool with inherent interface selectivity (Panel 1 on page 4). SFG provides information on the molecular structure, composition, charging state as well as on the molecular order of interfacial layers. Furthermore, in situ spectroscopy of project relevant interfaces is possible with SFG.^{10,11,14} In our project we want to restrict ourselves to aqueous electrolytes that contain no or very simple surfactants (such as photo-switchable amphiphiles) at concentrations well below their CMC. Substrates we want to study are Al_2O_3 single crystals with an adjustable concentration of atomically high steps.

2.3 Work program incl. proposed research methods

Work package (WP 1): Preparation and characterization of photo-switchable monolayers on oxide surfaces in and far outside equilibrium conditions (gas vs. liquid)

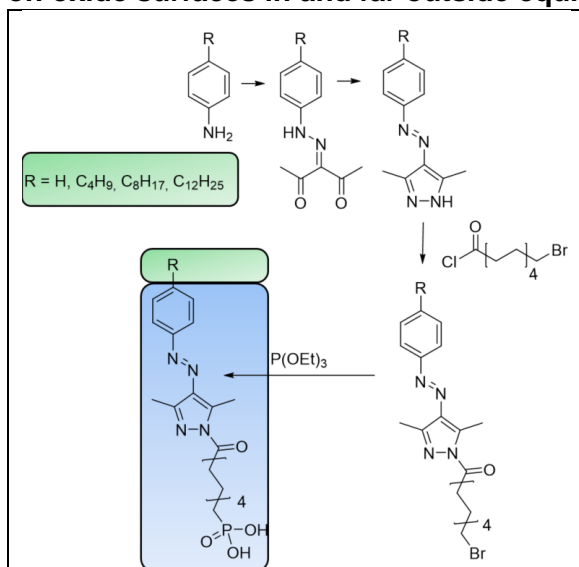


Figure 7 Structure and synthesis steps for AAP derivatives (blue shaded molecules) we propose to self-assemble at Al_2O_3 surfaces. $R = \text{H}$, butyl octyl and dodecyl groups.

Based on our earlier work and in strong collaboration with the group of Prof. Dr. Ravoo (Organic Chemistry Institute and Center for Soft Nanoscience, WWU Münster), we will synthesize in WP 1, AAP surfactants (Fig. 6) similar to the existing surfactant that is presented in Fig. 3c. Because our group and the Ravoo group have lab and office space (even at the same floor) within the Center for Soft Nanoscience (SoN) in Münster, the proposed collaboration and the exchange of molecules, samples and knowledge can be easily facilitated as the co-workers of both groups necessarily meet on a daily basis.

However, the surfactants needed for surface structuring in the proposed project will be modified with a phosphonic acid (PA) anchor group and different residues. As can be seen in Fig. 7 we propose in total 4 new molecules, which differ in their terminal alkyl residue.

The PA group is highly suitable for the formation of self-assembled monolayers on Al_2O_3 substrates because strong covalent bonds between the phosphonic acid anchors and the aluminum oxide substrate are formed. We have experimentally determined the Gibbs free energy for adsorption of octadecyl phosphonic acids on hydroxylated Al_2O_3 and is reported between -24 to -28 kJ/mol.¹⁰ This is well in line with earlier DFT simulations of the same system by Bauer et al.²⁵

Consequently, the PA molecules are irreversibly adsorbed on aluminum oxide substrates. Al_2O_3 is also a highly suitable substrate for the optical methods we want to apply (SFG and thin-film pressure balance) and which require that a mid-IR beam ($1000 - 4000 \text{ cm}^{-1}$) is transmitted through the substrate and that at least a reasonable large portion of the spectrum can be investigated. Because Al_2O_3 single crystals are available in high optical quality and provide a large spectral window in the mid-IR (cut off at 1700 cm^{-1}), aluminum oxides are beneficial compared to other

substrates like fused silica (cut off at 2800 cm^{-1}). Further, we¹⁷ and others²⁶ have shown that further modification of $\alpha\text{-Al}_2\text{O}_3(0001)$ crystals are possible by heating the substrates in an oxygen containing atmosphere, that leads to a transformation of a nanorough surface (that is caused by the polishing process) into atomically smooth surfaces. These exhibit well-defined steps with step-heights in molecular dimensions (0.2 nm^{17} , $1/12$ of the lattice constant along the c-axis). Depending on the miscut of the single crystals, different sizes of the atomically flat terraces can be generated. However, care must be taken to avoid step bunching when heating at high temperatures and for prolonged times.

Using substrates with different terrace size can be also used to intentionally introduce well-defined 2-dimensional defects (domain boundaries) in the SAMs. According to a recent MD study²⁷ on azo biphenyls on $\text{Au}(111)$, surface defects lead to a local reduction of the packing density and can be nucleation points that drive the monolayers response to light stimuli via cis/trans isomerization reactions.

As already discussed in the previous sections, the responsiveness of a photo-switchable monolayer decreases when the molecules become too closely packed inside the SAM. For that reason, we define as an additional goal in WP 1, to characterize the responsiveness of AAP phosphonic acid SAMs as a function of packing density and molecular structure of the AAP derivative. One way to change the packing density is as discussed already, the introduction of 2D defects by tuning the substrates' step concentration. Another approach without compromising the molecular order (but coverage) of a SAM, is to use mixed SAMs that comprise two different molecular species such as mixtures of AAP phosphonic acids (Fig. 7) and alkyl phosphonic acids. In the latter case, we can also use fluorinated molecules, which can help to determine the SAM composition and the molecular order of each species separately via SFG spectroscopy (C-D stretches $2000 - 2300\text{ cm}^{-1}$; C-H stretches $2800 - 3100\text{ cm}^{-1}$; C-F stretches $1300 - 1400\text{ cm}^{-1}$). This approach is similar to what we have used previously to stabilize C_{60} functionalized alkyl phosphonic acids in a SAM²⁸ or what has been previously reported for azobenzene SAMs on Au.⁸

For this SPP2171 project, we propose

- a. to introduce alkyl-phosphonic acids with different alkyl chain length such as C_6 , C_8 , C_{12} , C_{14} and C_{18} as well as to optimize the response of the mixed SAMs to light irradiation with the mixing ratio.
- b. To change the structure of the substrate structure (density of monoatomic high steps) by heating of single crystals with different miscuts.

For this we will systematically vary the mixing ratio and study the SAM performance for at least 4 mixing ratios per molecule using SFG spectroscopy and contact angle measurements. SFG spectroscopy of photo-responsive substrates in air can be performed with the light beams coming from the inert gas (our sample compartment can be purged with $\text{N}_2 5.0$) and the full spectral range can be used, while interfaces in contact with water can be only studied by transmitting, the laser beams through the substrate with limited IR transmittance (see above).

- i. For each sample and in each chemical environment (liquid vs dry gas phases) we want determine equilibrium structures for UV and visible light irradiation. Particularly in the gas phase, SFG provides direct structure information with different polarization combinations and from an analysis of CH_2 and CH_3 stretching vibrations of the terminal alkyl groups.
- ii. When brought in contact with water (macroscopic contact) we will address possible structure changes when the SAM layer adapts to its new chemical environment by recording time resolved SFG spectra.
- iii. The switching kinetics of each sample in air and in contact with water will be addressed with time resolved SFG spectroscopy on a molecular level. While measurements of the macroscopic contact angle during photo-switching of the substrates will reveal the wetting dynamics on larger length scales.

For the photo-responsive layer addressing C-H stretching modes with SFG is here again most informative, while changes in the water structure as a function of time can be studied by resolving O-H stretching bands with SFG. Note that the frequency of O-H stretching vibrations provides direct information of the strength and distribution of hydrogen bonds of interfacial water molecules. Typically broad O-H bands are observed where the low frequency branch (3200 cm^{-1}) in the spectrum is due to tetrahedrally coordinated 'ice like' water molecules at the interface, while the high frequency branch (3450 cm^{-1}) originates from more 'liquid like' water molecules at the interface.

WP 1: Collaborations and partners within SPP2171

Our approach to use $\alpha\text{-Al}_2\text{O}_3(0001)$ single crystals is also beneficial for a close comparison with possible simulations of layers with identical composition as they allow for a atomically-defined substrate structure. In fact, MD and kinetic Monte Carlo (MC) simulations are planned in the project by PD Dr. Svetlana Gurevic (Institute of Theoretical Physics, WWU Münster) and Prof. Dr. Andreas Heuer (Institute of Physical Chemistry, WWU Münster) where the dynamic behavior of AAP SAMs will be subject to intensive investigations. Within SPP 2171 we seek for strong collaboration with the Gurevic/Heuer groups.

WP 2: Mesoscopic characterization of thin films and drops in the absence and with very low surfactant concentrations

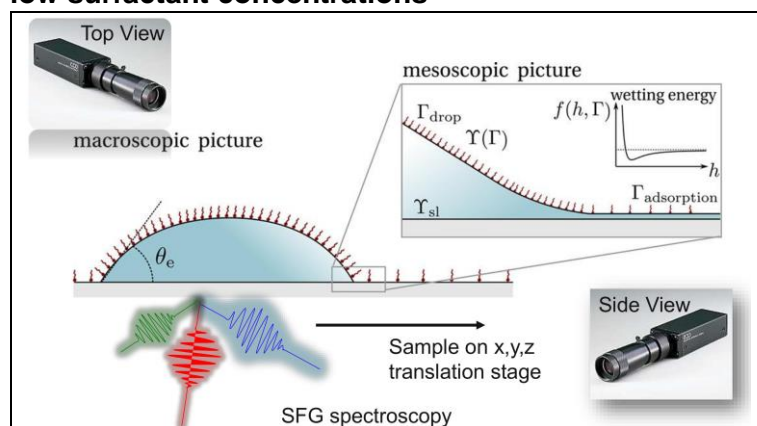


Figure 8 Macroscopic and mesoscopic picture of a drop in contact with a solid substrate and in the presence of surfactants. This image has been adapted from previous works by Thiele et al.²⁹ Using SFG spectroscopy the structure and composition can be locally determined by co-localized spectroscopy where the laser focus is moved through regions of interest parallel to the interface with high resolution. For localization of the laser spot within the drop and for simultaneous measurements of the dynamic contact angle and SFG spectra a second camera is installed. For this setup we request additional funding (cameras and objectives)

While the work in WP 1 with vibrational SFG spectroscopy was focused on the interfacial properties of fully wetted or dewetted interfaces, we want to increase the complexity of the systems by addressing the interfaces of aqueous drops on a photo-switchable substrate with SFG. For that, we study the wetting dynamics of drops that will be deposited on a photo-switchable substrate.

From WP 1, we will select at least 4 surface modifications that have shown moderate to high responsive behavior to light and address their interfaces inside the drop, far outside the drop and close to the 3-phase contact line. In our previous work,¹¹ on mechanical indentation of C_{18} -alkyl SAMs on Al_2O_3 we have already demonstrated that it is possible

to monitor the contact region by transferring the sample through the laser foci and to perform co-localized SFG spectroscopy. In this case, the SFG spectra will be normalized to the Fresnel coefficients of the individual environments (sample positions) which will account for the changes in linear optical properties such as changes in light reflectance and transmittance of the impinging fundamental and reflected SFG beams (see our earlier work^{1,10} on SAM dewetting where we have already used this approach).

Although the lateral resolution in our spectrometer is limited by the relative large diameters of the laser beams at the sample position ($\sim 600\text{ }\mu\text{m}$ at 804 nm and $\sim 500\text{ }\mu\text{m}$ for the tunable femtosecond IR pulse), the profile of the contact region as well as the molecular structure change inside the latter were well resolved in our earlier study.¹¹ Note, that resolution normal to the interface (interface selectivity) is independent of the size of the laser focus as the surface selectivity and sensitivity is driven by the SFG selection rules only (see Panel 1). To our best knowledge such co-

localized experiments on wetting drops with SFG where the relevant interfaces of the drop on a solid substrate have been studied as a function of lateral position and time (here after photo-switching of the surface layer) do not exist so far.

In WP 2, we will first establish a new measurement cell (Fig. 8), which will be a modification of the existing cells, but is equipped with two compact microscopes which allow for magnifications of ~40x or more and for which we request additional funding. This newly designed cell will allow us to determine the exact position of the laser focus with respect to the position of a previous deposited drop and with a second camera at the side of the cell, also the (dynamic) contact angle can be determined in situ by image analysis. The drop deposition will be performed with a syringe pump, which allows us to adjust the drop volume and the deposition speed in a well-defined way.

- a. The experiments in WP 2 will be performed first at drop interfaces in equilibrium which is established is either by prolonged exposure to UV light in order to achieve predominant cis isomerization of the surface layer or prolonged exposure to visible light (for AAPs even 520 nm is possible) to achieve predominantly trans isomerization of the surface layer. For all experiments with SFG, vibrational spectra of C-H and O-H stretching vibrations will be recorded and provide local information on the structure of the AAP SAM. This is achieved by scanning the laser focus from the interior of the drop to the exterior.
- b. Once the initial equilibrium properties have been determined, non-equilibrium properties are studied in a second set of experiments. For that, we will perform time-resolved SFG experiments at selected positions of the drop (interior, exterior and close to the three-phase contact line) and synchronize the spectra acquisition to the imaging of the drop shape using the camera at the side of the cell. This will deliver us with the change of the contact angle and the change of interfacial molecular structure in one experimental run.
- c. In addition to the wetting dynamics of a photo-switchable substrate in contact with pure water, we are also planning to introduce low molecular weight amphiphiles like those we have been discussing in Figure 3 and 4. This will enable us to fine tune the switching behavior and to address the wetting dynamics also in the presence of surfactants. In addition, this work in c) will enable us also to address also possible surfactant gradients at the mesoscopic scale – A topic that has been recently addressed by Thiele et al.^{29,30} (see also Fig. 8, which was adapted from that work²⁹). In this respect we will share our experimental results and collaborate with Prof. Dr. Uwe Thiele (Institute of Theoretical Physics, WWU Münster) and his co-workers.

Collaborations and partners within SPP2171 and WP 2

In a SPP2171 project on drops and films of simple liquids and dilute surfactant solutions on adaptive substrates, Thiele plans to apply and further develop a gradient dynamics approach to thin-film models that was described previously.^{29–31} Within this approach, the wetting dynamics on photo-switchable substrates shall be considered as a limiting case of adaptation. As the latter project by Thiele, directly relates to the work planned in our project, we plan to collaborate with Thiele and co-workers in order to combine their theoretical modelling approaches with our experiments.

Besides collaboration with SPP2171 projects that concentrate on simulations, we will also make our setup available to other experimentally working groups with SPP2171. Particularly, we seek collaborations with SPP2171 projects, where experiments on molecular structure changes of relevant interfaces of drops and films on photo-switchable but also adaptive surfaces need to be addressed. In this respect, we will collaborate the SPP2171 project of Prof. Dr. Bart Jan Ravoo (WWU Münster) and perform in situ characterization with SFG using the setup for dynamic wetting described above. Within the Ravoo SPP2171 project, photo-responsive SAMs but also photo-responsive polymer brushes will be made by precision synthesis, self-assembly and contact printing. The latter systems are of particular interest, because they show increased complexity compared to what is proposed in our project (see Fig. 7) and fall not only in one focal area of SPP2171, but actually into two – adaptive and (photo-)switchable substrates. That is because we expect that AAP polymer brushes will adapt to different chemical environments, which can be suspected

from previous works, but in the case of AAP brushes the wetting dynamics can be additionally changed by light irradiation. Such a combination has been to the best of our knowledge not studied so far and will require detailed (molecular) level characterization which will be performed within WP2 of our project.

Additionally we plan to collaborate with the SPP2171 by Prof. Dr. Regine von Klitzing (TU Darmstadt). Here, the spectroscopic setup which is developed in our WP 2, will be used to address the wetting dynamics and molecular structure changes of PNIPAM microgels as well of PSS/PDADMAC polyelectrolyte multilayers (PEM). Previously, von Klitzing and co-workers³² have shown that a complex interplay between polyelectrolyte backbone and charge density determines the wetting behavior of PEMs. The use of SFG spectroscopy to study the wetting dynamics in PEM is, therefore, interesting because changes in the interfacial charging state (via the O-H stretching modes, see Panel 1 and discussion of Fig. 4) as well as in the structure of polyelectrolytes and water at the interfaces (see our earlier work^{33,34}) can be addressed in situ and resolved in real time. Using the proposed setup (Fig. 8) we will address PEM that are relevant for SPP2171 project of Prof. Dr. Regine von Klitzing.

WP 3: Wetting dynamics of photo-switchable layers with well-defined periodicity

In addition to the preparation and characterization of molecular structure changes and wetting dynamics on extended photo-switchable substrates with (mixed) AAP SAMs, we will micro and nano pattern the oxide surfaces with photo-switchable moieties using contact printing and nanoimprint lithography. The latter will be done within our SPP2171 collaboration with Prof. Dr. Bart Jan Ravoo (WWU Münster). Within WP 2, we will concentrate on stripe pattern with defined periodicities at the nano (a few hundred nm) and micrometer scale (a few μm to several hundred μm). In Fig. 4 we presented already two examples with stripes that a lateral width of 150 and 10 μm . These substrates were already produced in the Ravoo group using the contact printing method. In WP 2 we will also apply Al_2O_3 single crystals as substrates where we will print striped layers of the AAP derivatives (Fig. 6) and their mixtures with alkyl and fluorinated phosphonic acids that are followed by stripes of the undecorated Al_2O_3 substrate. This way, we can laterally modify the interface tension and thus spatially localize the light stimulated response of the substrate.

- a. We will apply SFG spectroscopy to address equilibrium and non-equilibrium properties of striped AAP layers and compare the results with the information obtained in WP 1 and 2. Experiment will be done initially in the gas phase and then extended to wetting drops where the setup of WP 2 (visual inspection from the top and the side as well as SFG from the bottom) is done.
- b. In a second, set of experiments we will determine the wetting dynamics similar to the experiments proposed in WP 2b.
- c. We prepare individual drops on a single stripes as well as between neighboring stripes and observe their behavior (see preliminary work shown in Fig. 5) as a function of light stimulus and switching frequency.

Further collaborations with the SPP2171 and WP3 of this project

Experiments in WP3 c. (see above) will be supported by simulations using mesoscopic continuum models of drops on patterned surfaces. Our collaborators PD Dr. Svetlana Gurevich and Prof. Dr. Andreas Heuer and their co-workers at University Münster will perform simulations (see corresponding SPP 2171 proposals).

Table 1 Time table and work plan for a 36 month project

	1-12		13-24		25-36	
WP 1 Perform synthesis and study the responsiveness of R-AAP-PA SAMs using different mixing ratios with C8, C14, C18 alkyl phosphonic acids (inert gas vs. water)						
WP 2 Construct and build an optimized measurement cell (Fig. 8) for co-localized SFG and dynamic contact angle measurements						
WP 2: Select 4 samples from WP 1 with high to intermediate switchability and perform experiments with co-localized SFG at the drop-switchable substrate interface						
WP2: Add additional low molecular weight surfactants at concentration below their CMC and characterize dynamic wetting on a photo-switchable substrate						
WP3: Print structured photo-switchable substrates with different strip patterns and characterize the wetting dynamics upon photo-switching using SFG, the thin-film pressure balance and in situ microscopy						
Prepare a project report						

2.4 Data handling

The information and results from this project will be stored in an institute internal database and will be published in peer reviewed journals preferably with the possibility of open access for which we request additional funds (see below). Furthermore, we will present our work on scientific conferences with international outreach, so that the results can be made available to a broader audience.

2.5 Other information

N/A

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

N/A

3 Bibliography

- (1) Meltzer, C., Dietrich, H., Zahn, D., Peukert, W., Braunschweig, B. Self-Assembled Monolayers Get Their Final Finish via a Quasi-Langmuir–Blodgett Transfer. *Langmuir* **2015**, 31, 4678–4685.
- (2) Groten, J., Bunte, C., R  he, J. Light-induced switching of surfaces at wetting transitions through photoisomerization of polymer monolayers. *Langmuir* **2012**, 28, 15038–15046.
- (3) Guo, F., Guo, Z. Inspired smart materials with external stimuli responsive wettability: a review. *RSC Advances* **2016**, 6, 36623–36641.
- (4) Xin, B., Hao, J. Reversibly switchable wettability. *Chem. Soc. Rev.* **2010**, 39, 769–782.
- (5) Moldt, T., Brete, D., Przyrembel, D., Das, S., Goldman, J. R., Kundu, P. K., Gahl, C., Klajn, R., Weinelt, M. Tailoring the Properties of Surface-Immobilized Azobenzenes by Monolayer Dilution and Surface Curvature. *Langmuir* **2015**, 31, 1048–1057.
- (6) Moldt, T., Przyrembel, D., Schulze, M., Bronsch, W., Boie, L., Brete, D., Gahl, C., Klajn, R., Tegeder, P., Weinelt, M. Differing Isomerization Kinetics of Azobenzene-Functionalized Self-Assembled Monolayers in Ambient Air and in Vacuum. *Langmuir* **2016**, 32, 10795–10801.

- (7) Kwon, G., Panchanathan, D., Mahmoudi, S. R., Gondal, M. A., McKinley, G. H., Varanasi, K. K. Visible light guided manipulation of liquid wettability on photoresponsive surfaces. *Nature Communications* **2017**, *8*, 14968 EP -.
- (8) Valley, D. T., Onstott, M., Malyk, S., Benderskii, A. V. Steric Hindrance of Photoswitching in Self-Assembled Monolayers of Azobenzene and Alkane Thiols. *Langmuir* **2013**, *29*, 11623–11631.
- (9) Yu, X., Wang, Z., Jiang, Y., Shi, F., Zhang, X. Reversible pH-Responsive Surface: From Superhydrophobicity to Superhydrophilicity. *Adv. Mater.* **2005**, *17*, 1289–1293.
- (10) Meltzer, C., Yu, H., Peukert, W., Braunschweig, B. Molecular structure of octadecylphosphonic acids during their self-assembly on α -Al₂O₃(0001). *Phys. Chem. Chem. Phys* **2018**, *20*, 19382–19389.
- (11) Meltzer, C., Paul, J., Dietrich, H., Jäger, C. M., Clark, T., Zahn, D., Braunschweig, B., Peukert, W. Indentation and self-healing mechanisms of a self-assembled monolayer - A combined experimental and modeling study. *J. Am. Chem. Soc.* **2014**, *136*, 10718–10727.
- (12) Pathak, A., Bora, A., Braunschweig, B., Meltzer, C., Yan, H., Lemmens, P., Daum, W., Schwartz, J., Tornow, M. Nanocylindrical confinement imparts highest structural order in molecular self-assembly of organophosphonates on aluminum oxide. *Nanoscale* **2017**, *9*, 6291–6295.
- (13) Sauerbeck, C., Braunschweig, B., Peukert, W. Surface charging and interfacial water structure of amphoteric colloidal particles. *J. Phys. Chem. C* **2014**, *118*, 10033–10042.
- (14) Engelhardt, K., Peukert, W., Braunschweig, B. Vibrational sum-frequency generation at protein modified air-water interfaces: Effects of molecular structure and surface charging. *Curr. Opin. Colloid. Interface Sci.* **2014**, *19*, 207–215.
- (15) Richmond, G. L. Molecular bonding and interactions at aqueous surfaces as probed by vibrational sum frequency spectroscopy. *Chem. Rev.* **2002**, *102*, 2693–2724.
- (16) Shen, Y. R., Ostroverkhov, V. Sum-frequency vibrational spectroscopy on water interfaces: polar orientation of water molecules at interfaces: Chemical Reviews. *Chem. Rev.* **2006**, *106*, 1140–1154.
- (17) Braunschweig, B., Eissner, S., Daum, W. Molecular Structure of a Mineral/Water Interface: Effects of Surface NanoRoughness of α -Al₂O₃ (0001): The Journal of Physical Chemistry C. *J. Phys. Chem. C* **2008**, *112*, 1751–1754.
- (18) Butt, H.-J., Berger, R., Steffen, W., Vollmer, D., Weber, S. A. L. Adaptive Wetting—Adaptation in Wetting. *Langmuir* **2018**.
- (19) Schnurbus, M., Stricker, L., Ravoo, B. J., Braunschweig, B. Smart Air–Water Interfaces with Arylazopyrazole Surfactants and Their Role in Photoresponsive Aqueous Foam. *Langmuir* **2018**, *34*, 6028–6035.
- (20) Weston, C. E., Richardson, R. D., Haycock, P. R., White, A. J. P., Fuchter, M. J. Arylazopyrazoles: azoheteroarene photoswitches offering quantitative isomerization and long thermal half-lives. *J. Am. Chem. Soc.* **2014**, *136*, 11878–11881.
- (21) Stricker, L., Fritz, E.-C., Peterlechner, M., Doltsinis, N. L., Ravoo, B. J. Arylazopyrazoles as Light-Responsive Molecular Switches in Cyclodextrin-Based Supramolecular Systems. *J. Am. Chem. Soc.* **2016**, *138*, 4547–4554.
- (22) Moratz, J., Stricker, L., Engel, S., Ravoo, B. J. Controlling Complex Stability in Photoreversible Macromolecular Host-Guest Systems: Toward Reversible Capture of DNA by Cyclodextrin Vesicles. *Macromol. Rapid Commun.* **2017**.
- (23) D. Exerowa, P. M. Kruglyakov, Eds. *Foams and Foam Film, Theory Experiment, Application in: Studies in Interface Science*, D. Möbius and R. Miller eds. in D. Möbius, R. Miller; Elsevier, 1998.
- (24) Stubenrauch, C., Klitzing, R. von. Disjoining pressure in thin liquid foam and emulsion films - New concepts and perspectives. *J. Phys. Cond. Mat.* **2003**, *15*, R1197-R1232.

- (25) Bauer, T., Schmaltz, T., Lenz, T., Halik, M., Meyer, B., Clark, T. Phosphonate- and Carboxylate-Based Self-Assembled Monolayers for Organic Devices: A Theoretical Study of Surface Binding on Aluminum Oxide with Experimental Support. *ACS Applied Materials & Interfaces* **2013**, 5, 6073–6080.
- (26) Ribič, P. R., Bratina, G. Behavior of the (0 0 0 1) surface of sapphire upon high-temperature annealing. *Surf. Sci.* **2007**, 601, 44–49.
- (27) Cantatore, V., Granucci, G., Rousseau, G., Padula, G., Persico, M. Photoisomerization of Self-Assembled Monolayers of Azobiphenyls: Simulations Highlight the Role of Packing and Defects. *J. Phys. Chem. Lett* **2016**, 7, 4027–4031.
- (28) Rumpel, A., Novak, M., Walter, J., Braunschweig, B., Halik, M., Peukert, W. Tuning the molecular order of C60 functionalized phosphonic acid monolayers: *Langmuir*. **2011**, 27, 15016–15023.
- (29) Thiele, U., Snoeijer, J. H., Trinschek, S., John, K. Equilibrium Contact Angle and Adsorption Layer Properties with Surfactants. *Langmuir* **2018**, 34, 7210–7221.
- (30) Thiele, U. Recent advances in and future challenges for mesoscopic hydrodynamic modeling of complex wetting. *Coll. Surf. A* **2018**, 553, 487–495.
- (31) Thiele, U., Archer, A. J., Pismen, L. M. Gradient dynamics models for liquid films with soluble surfactant. *Phys. Rev. Fluids* **2016**, 1, 83903.
- (32) Hänni-Ciunel, K., Findenegg, G. H., Klitzing, R. von. Water Contact Angle On Polyelectrolyte-Coated Surfaces: Effects of Film Swelling and Droplet Evaporation. *Soft Materials* **2007**, 5, 61–73.
- (33) Schulze-Zachau, F., Bachmann, S., Braunschweig, B. Effects of Ca²⁺ Ion Condensation on the Molecular Structure of Polystyrene Sulfonate at Air–Water Interfaces. *Langmuir* **2018**, 34, 11714–11722.
- (34) Schulze-Zachau, F., Braunschweig, B. Structure of Polystyrenesulfonate/Surfactant Mixtures at Air–Water Interfaces and Their Role as Building Blocks for Macroscopic Foam. *Langmuir* **2017**, 33, 3499–3508.

4 Requested modules/funds

Explain each item for each applicant (stating last name, first name).

4.1 Basic Module

4.1.1 Funding for Staff

Doctoral researcher (75 % TVL-E13)

36 Months

Experiments in this project will be performed by a doctoral candidate (DC) at our institute. These experiments are highly demanding as they can be only performed by highly qualified researchers that have experience in laser spectroscopy. For the proposed project, the DC will fully dedicate his or her working time to this project and will also document the results in peer reviewed international journals and present the work on national and international conferences as well as on SPP2171 organized conferences and internal workshops. The DC will also work on the further development of the existing experimental setup as outlined in WP 2.

4.1.2 Direct Project Costs

Equipment up to Euro 10,000, Software and Consumables

XBO lamp for Zeiss microscope attached to the TFPB (type XBO 75 W/2 OFR); MS Scientific (limited life time of 200 h, 198 € per lamp, we need 5)	990 €
α -Al ₂ O ₃ (0001) single crystals as windows with 25mm diam.(+/-0.10mm) Thickness: 3 mm (+/-0.05mm) Surface Roughness: Ra <0.5 nm Both sides epi-polished (6 pieces with 87 € each) and 10 Substrates Size: 10 x 10mm (+/-0.1mm) Thickness: 3 mm (+/-0.05mm) Surface Roughness: Ra <0.5 nm (43 € per piece)	950 €
5x Infrasil window (fused silica) for works with PEM in WP2 (93 €/piece)	465 €
Replacement for UV (75 € per LED with limited life time) and green LEDs	380 €
Supply of lab gases (N ₂ , Ar) for purging the liquid solutions and the beam path of the femtosecond IR pulse	800 €
Cooling fluid for laser spectrometer and particle filters	
C ₆ , C ₈ , C ₁₂ , C ₁₄ , C ₁₈ alkyl phosphonic acids (1 g 66 € for each, 3x 1g, Merck)	990 €
Fluorinated phosphonic acids from Merck: C ₈ H ₆ F ₁₃ O ₃ P (2 g, 339 €), C ₁₀ H ₆ F ₁₇ O ₃ P (1 g, 443 €), C ₁₂ H ₆ F ₂₁ O ₃ P (0.5 g, 404 €)	1,200 €
Adaptation of the existing SFG setup (sample compartment) for visual inspection of the wetted surface area and local control of the gas phase composition. Small parts from mechanical workshop 150 €, modular microscope that can be integrated in the sample compartment (Edmund Optics objective 340 € x2), CMOS cameras (1065 € x2) posts and holders for optics	2,960 €
Chemicals for synthesis of AAPs as proposed in Fig. 7 4-Butylanilin (100 g, 72 €), 4-Octylanilin (61 €/g, 3x), 4-Dodecylanilin (5 g, 224 €) NaNO ₂ (>97%, 100 g, 34 €), NaOAc (250 g, 50 €), HCl (>37%, 500 mL, 57 €), EtOH (abs. >99.8%, 1 L, 205 €), N ₂ H ₄ (35 wt.% in H ₂ O, 36 €), 10-Bromodecanoic acid (>95%, 78 €/ 5g, 2x), SOCl ₂ (>99 %, 5 mL, 25 €), Triethylphosphite (98%, 5 mL, 20 €), EtOAc for column chromatography (>99.7 %, 2 x 2.5 L, 231 €) MeOH for column chromatography (>99.9 %, 1 x 2.5 L, 63 €), THF for column chromatography (>99.9 %, 1x 1 L, 161 €) Total: 1,550 € x2	3100 €
General lab requirements: gloves, tubes, pipette tips etc., chemicals for cleaning of substrates and glassware (Alconox, Nochromix, 98 % H ₂ SO ₄) (200 € / month)	7,200 €
Production of high purity water: filters, UV lamps, disinfection chemicals (Millipore, Merck). Cooling fluid and filters for laser spectrometer	1,300 €
Sum incl. VAT 20,335 €	

4.1.2.1 Travel Expenses

We believe that for publication and for an increase of the visibility of the results obtained from this project, participation at the following national and international conferences is required.

- 1st and 2nd year: one SPP workshop where DC and PIs are present (4 days per workshop) 80 € per day plus 200 Euro travel costs 2,080 €
 - 1st year: Advanced School within SPP where DC is present (5 days) 600 €
 - 2nd year: Phd candidate workshop organised by themselves where all employed researchers should be present (4 days) 520 €
 - International conference – DC student and PI are present (5 days) 1,200 €
 - Meeting of the European Colloid and Interface Society 2021 1,600 €
- Travel costs total 6,000 €**

4.1.2.2 Project-related publication expenses

Cost for open access publication in peer reviewed journals 2,250 €

Sum of all direct costs in 4.1.2. 28,585 €

5 Project requirements

5.1 Employment status information

Prof. Dr. Björn Braunschweig (W1 tenure track W2, Neuberufung 01.01.2017)
Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster

5.2 Composition of the project group

Prof. Dr. Björn Braunschweig (PI)
Frau Gönül Acga (Physikalisch technische Assistentin)
N.N., Christian Honnigfort and Marco Schnurbus

5.3 Cooperation with other researchers

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

We plan to collaborate with the SPP2171 with the following researchers. For a full description of the planned research and details on the collaboration we refer to the discussion. Below we will give the page numbers where the individual collaborations are discussed in detail in the text.
PD Dr. Svetlana Gurevic, Institute of Theoretical Physics, WWU Münster (Pages: 13 and 15)
Prof. Dr. Andreas Heuer, Institute of Physical Chemistry, WWU Münster (Pages: 13 and 15)
Prof. Dr. Bart Jan Ravoo, Organic Chemistry Institute, WWU Münster (Pages, 11, 14 and 15; as well as previous work)
Prof. Dr. Regine von Klitzing, Soft Matter Interfaces, TU Darmstadt (Pages 14 and 15)
Prof. Dr. Uwe Thiele, Institute of Theoretical Physics, WWU Münster (Page: 14)

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

Prof. Dr.-Ing. Wolfgang Peukert, Institute of Particle Technology (LFG), FAU Erlangen-Nürnberg
Prof. Dr. Tim Clark and (Theoretical and computational chemistry), FAU Erlangen-Nürnberg
Prof. Dr. Dirk Zahn (Theoretical and computational chemistry), FAU Erlangen-Nürnberg
Prof. Dr. Robin Klupp Taylor, Institute of Particle Technology (LFG), FAU Erlangen-Nürnberg
Prof. Dr. Marc Tornow, TU München, Chair for Nanoelectronics
Prof. Dr. Sannakaisa Virtanen, Chair of Surface Science and Corrosion, FAU Erlangen-Nürnberg
Prof. Dr. Dana D. Dlott, Chemistry, University of Illinois at Urbana-Champaign, USA

5.4 Scientific equipment

- Homebuilt SFG spectrometer with Spectra Physics Solstice Ace laser system (1 kHz, >7 mJ) and Light Conversion Topas and NDFG unit (1 – 20 μm), sample stage with xyz positioning system, Andor Newton EMCCD and Andor Kymera spectrograph (1200 and 1800 l/mm gratings).
- Bruker Vertex 70 FTIR spectrometer including a homebuilt thin-film pressure balance
- Thin-film pressure balance with Zeiss Microscope Axio Imager A2m with XBO lamp and Avantes ULS3648 ultra low stray light fiber optic UV/Vis/NIR spectrometer for white light interferometry
- Millipore purification system for ultra-pure water (TOC<5 ppb, >18 M Ωcm)
- 2 Tensiometers: PAT1M from Sinterface and Krüss DSA100 (including rotation unit).
- Lambda 650 Perkin Elmer UV/Vis spectrometer
- Within the Center of Soft Nanoscience we have access to AFM, ToF-SIMS and XPS.