

## SPP 2171 Dynamic wetting of flexible, adaptive and switchable substrates

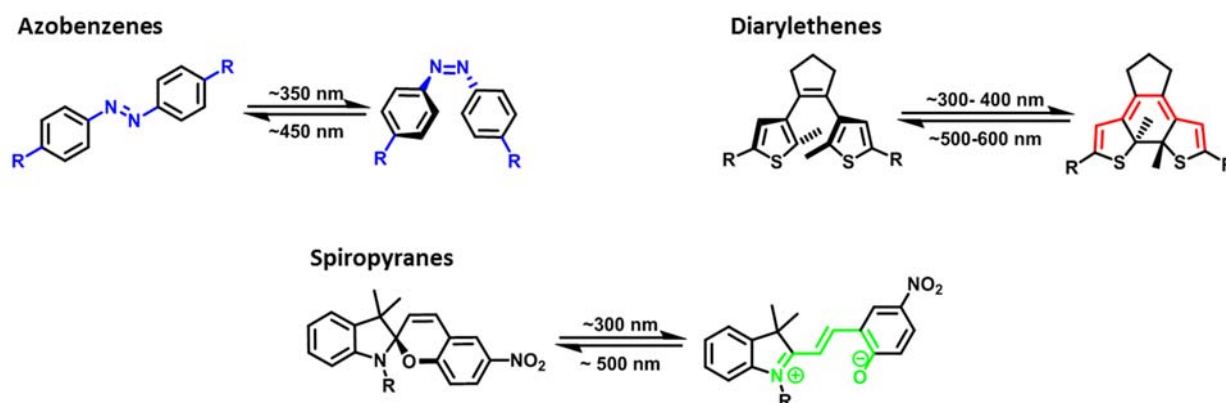
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### Dynamic wetting of self-assembled monolayers and polymer brushes functionalized with photoresponsive arylazopyrazoles

## Project Description

### 1 State of the art and preliminary work

Light is a particularly attractive external stimulus to modify surface properties since it can be applied with very high local and temporal resolution. Molecular switches such as azobenzenes (1), diarylethenes (2) and spiropyranes (3) (Figure 1) have been explored in a range of photo-responsive coatings and materials in which the photo-isomerization of the nanoscale switch induces a macroscopic effect such as a change of stability, permeability or indeed wettability (4). In view of the substantial change in polarity that occurs upon photoisomerization, it is not surprising that azobenzenes and (less frequently) spiropyranes have been immobilized on a broad range of surfaces to obtain photoswitchable wettability. Since the trans-isomer of the azobenzene is much less polar than the cis-isomer and the closed isomer of the spiropyrane is much less polar than the open isomer (Figure 1), photoisomerization of these molecular switches on surfaces typically results in a substantial and reversible change of wettability. To this end, photoswitches are either adsorbed as self-assembled monolayers (SAMs, 5-14) or embedded into polymer brushes grown from the surfaces (15-22). A comprehensive review of these studies is beyond the scope of this proposal, but a number of important findings are highlighted in the following paragraph.



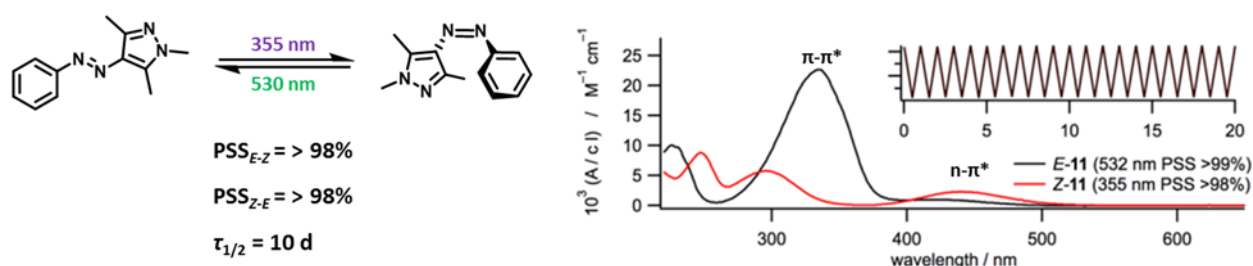
**Figure 1. Molecular structures of the most common classes of photoswitches.** Azobenzenes are photoisomerized between the trans-isomer and the cis-isomer which have different shape and polarity. Diarylethenes are photoisomerized between an open and a closed form which have similar shape but very different conjugation. Spiropyranes are photoisomerized between a closed and neutral spiro-isomer and an open and zwitterionic merocyanine form.

Regarding SAMs of azobenzenes, Delorme et al (6) were among the first to measure photoswitchable wettability of SAMs on silicon surfaces and Pei et al (11) showed that the photoswitchable wettability depends critically on the molecular packing and density of the SAM. Groten et al (12) reported that using a substrate with a nanoscale roughness ("black silicon") the

photoswitched wettability can be dramatically enhanced to provide a reversible change in contact angle of more than 150 degrees upon irradiation. A similar effect had previously been observed for a SAM of fluorinated azobenzenes on a nanoporous surfaces (9). In a very elegant study, Wan et al (8) described a supramolecular approach to photoswitchable wettability based on a photoresponsive inclusion complex of azobenzene and  $\alpha$ -cyclodextrin. Recently, Chen et al (13) showed that also synthetic molecular motors can be immobilized in SAMs to provide photoswitchable wettability. The photoswitchable wettability of polymer brushes containing azobenzenes was studied by Yuan et al (15) and Sun et al (22). Enhanced wettability changes were observed for brushes grown on rough surfaces such as mats of electrospun fibers (18). Photoswitchable wettability was also observed for polymer brushes functionalized with spiropyranes (16, 19).

However, current approaches for the photoswitching of surface wettability still face significant limitations. Many molecular switches are rather difficult to synthesize and/or immobilize, the fatigue resistance of diarylethenes and spiropyranes is poor, the change in wettability induced by photoswitching is often modest unless a nanorough substrate is used (9, 12), and in particular, the highly popular azobenzenes suffer from a restricted photoresponse due to the unfavorable photostationary state. For many azobenzenes, only about 50% of the switches effectively switch upon irradiation because of a significant overlap of the bands for the trans-isomer and cis-isomer (1). On the basis of these observations, **it is evident that enhanced photoswitchable wettability has much to gain from the development of new molecular photoswitches.**

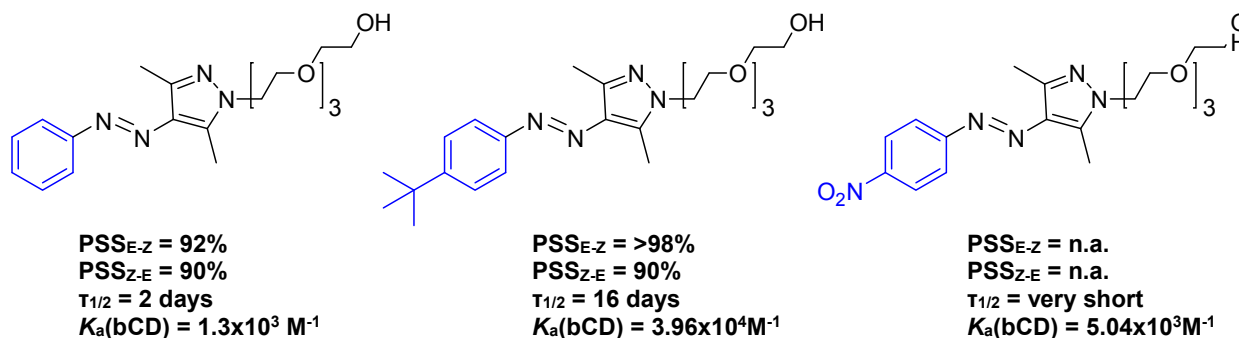
To address the shortcomings of the current generation of molecular photoswitches, several groups have developed variations of azobenzenes with significantly improved photophysical properties. The introduction of four ortho-substituents such as methoxy (23) and fluorine (24) results in a red shift of the  $n\text{-}\pi^*$  band, so that the band overlap for the trans-isomer and the cis-isomer is significantly decreased, the photostationary state increases to more than 90 %, and the cis-trans photoisomerization can be induced with green or even red light. Alternatively, the introduction of N-heterocycles that replace one of the benzene rings of azobenzene results in equally important improvements of the photophysical properties. In this area, Herges et al (25) have developed arylazopyridines and arylazoimidazoles (benzene replaced by pyridine or imidazole), König et al (26) reported arylazoindazoles (benzene replaced by indazole) and Fuchter et al (27) have described arylazopyrazoles (AAPs, benzene replaced by pyrazole). In the seminal paper by Fuchter et al (27a), it was shown that methyl substituted AAPs can be photoisomerized using UV light (360 nm) and green light (530 nm) irradiation with a very favourable photostationary state (>98 % in both directions), very slow thermal relaxation of the cis-isomer (half-life > 10 days) and very good fatigue resistance. Important properties of the AAPs are highlighted in Figure 2.



**Figure 2. Arylazopyrazole (AAP) photoswitch reported by Fuchter et al.** This photoswitch has little band overlap between the  $\pi\text{-}\pi^*$  and the  $n\text{-}\pi^*$  band resulting in a very favorable photostationary state in both directions. In addition, the thermal relaxation of the cis-isomer is very slow, and the fatigue resistance is very high. Data taken from Fuchter et al (27a).

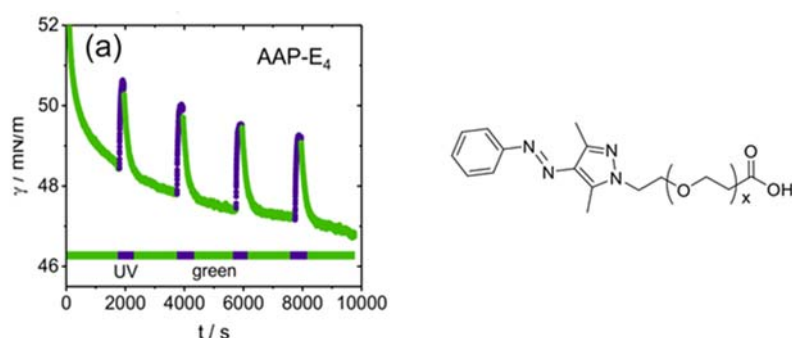
We have recently shown that a wide range of water-soluble AAP derivatives can be easily synthesized, and we have shown that depending on the substitution pattern, they can be isomerized with more than 95% efficiency while the thermal stability of the *cis*-isomer can be tuned from high to low (Stricker JACS 2016 and Stricker CEJ 2018). A selection of water-soluble

AAP derivatives and some key properties are shown in Figure 3. In our follow-up work, we have shown that (similar to azobenzenes) also AAPs with a wide range of substituents on the benzene ring can form photoresponsive host-guest complexes with beta-cyclodextrin in aqueous solution, since the less polar trans-isomer forms a much more stable inclusion complex than the more polar cis-isomer ([Stricker JACS 2016](#) and [Stricker CEJ 2018](#)). DFT calculations show that the dipole moment of trans-AAP is less than the dipole moment of cis-AAP. It should be noted that the dipole moment of both isomers depends on the substitution of the AAP, so that also the polarity difference of the two isomers can vary rather strongly depending on the substituents.



**Figure 3. Key properties of selected water-soluble AAPs.** Alkyl substituents such as *t*-butyl reduce the thermal relaxation and enhance the affinity for beta-cyclodextrin. Strongly electron withdrawing substituents such as nitro lead to a push-pull system with very fast relaxation of cis to trans. Data taken from [Stricker CEJ 2018](#).

Since then, we have also shown that the AAP-beta-cyclodextrin complexation is a versatile and powerful photoresponsive non-covalent interaction motif that can be used in a wide range of soft materials and interfaces. Important examples include the photocontrolled stiffening, softening and payload release from peptide hydrogels with photoresponsive crosslinks based on the AAP-beta-cyclodextrin pair ([Chu ChemComm 2017](#)) and the photocontrolled clustering of cyclodextrin-coated nanoparticles induced by AAP crosslinkers ([Engel Small 2018](#)). Together with Prof. Björn Braunschweig in Münster we have also shown that amphiphilic AAPs can adsorb on the air-water interface and that their surface activity is photoresponsive since trans-AAP is more surface active than cis-AAP ([Schnurbus Langmuir 2018](#)). Consequently, alternating irradiation with UV and green light results in a reversible change of surface tension (Figure 4). The self-assembly of AAP amphiphiles on the interface was investigated with sum frequency generation (SFG) spectroscopy. Furthermore, the molecular photoisomerization resulted in a macroscopic destabilization of foams. In follow-up work, we have observed that the surface activity of the AAP derivatives can be significantly enhanced using molecular modification of the AAP with additional hydrophobic substituents as well as different hydrophilic head groups such as ammonium and sulfonate. These findings clearly demonstrate that AAP are promising candidates for the preparation of photoresponsive surfaces and interfaces and that their interfacial properties can be fine-tuned by molecular design.

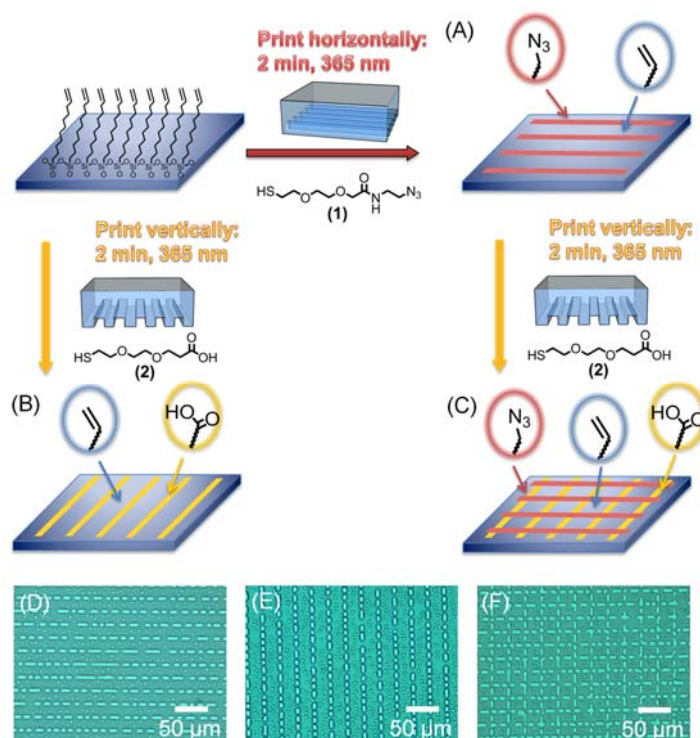


**Figure 4. Photoresponsive surface activity of an amphiphilic AAP derivative ( $x = 4$ ).** Dynamic surface tension measurements under alternating irradiation with green and UV light. Data taken from [Schnurbus et al. 2018](#).

In the framework of this project, we aim to investigate the dynamic wetting of surfaces modified with AAP photoswitches. Although we have not investigated this topic to date, we have published two reports that show that in principle AAPs can be immobilized on various surfaces and the molecular properties of the photoswitch can give rise to dynamic and reversible phenonemena at the solid-liquid interface. In the first report, we have incorporated AAPs into hydrophilic polymer brushes that were grown on silica microparticles ([Sagebiel ChemComm 2017](#)). Using cyclodextrin-coated magnetite nanoparticles, we could assemble these microparticles into colloidal molecules ("supraparticles") with dual response to light and magnetic field due to the photoresponsive AAP-beta-cyclodextrin interaction and the magnetization of the superparamagnetic nanoparticles. In the second report, AAPs were immobilized in the form of inclusion complexes of cucurbituril[8] and the photoresponsive surface was used for the light-directed adhesion of cells ([Wiemann CEJ 2018](#)). To the best of our knowledge, there are no reports on the immobilization of AAPs and/or the properties of the resulting photoresponsive surfaces beyond these two papers by our own group.

Surface patterning will be an important aspect of this project and although even a succinct overview of the potential "hard" photolithography and alternative "soft" lithography methods available to make patterned molecular surface layers is clearly beyond the scope of this project proposal, a few important methods and preliminary results regarding the patterning of functional SAMs and polymer brushes will be described in the following paragraphs. Among the various methods of soft lithography (28), microcontact printing is arguably the most versatile one for the patterning of functional SAMs. Microcontact printing is an additive patterning method that involves the local deposition of a monolayer of "ink" molecules on a substrate of choice by means of an elastomeric stamp (typically: poly(dimethyl siloxane), PDMS) with a relief microstructure. The ink may consist of a low molecular weight compound, a polymer, or even a protein or a nanoparticle. The substrate can be nearly any hard or soft material. The ink may adhere to the substrate by any physical or chemical interaction and the soft nature of the stamp ensures conformal contact and faithful pattern transfer from the stamp to the substrate.

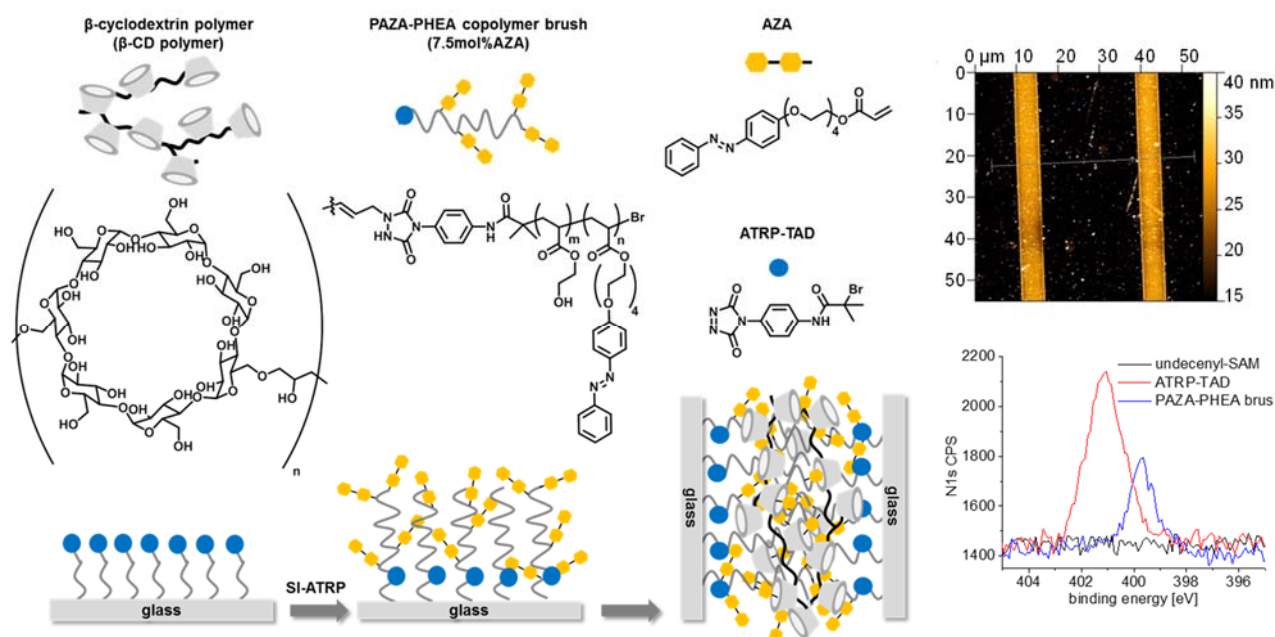
In recent years, we have used microcontact printing to prepare a wide range of functional SAMs in particular by inducing chemical reactions in the contact areas between the stamp and the substrate. A representative example is shown in Figure 5. In this example ([Wendeln CEJ 2012](#)), glass substrates and silicon wafers were first coated with a SAM of alkenyl terminated silane. Microcontact printing was then used to print various bifunctional inks in line patterns. Since the inks were typically more hydrophilic than the alkene terminated SAM, microcontact printing resulted in distinct wetting patterns when the surface was exposed to water vapor. Using dynamic contact angle measurements, we have shown that the water contact angle is reduced from ca. 100 degrees for the alkyl terminated SAMs to less than 40 degrees for the SAM modified by thiol-ene reaction. Using follow-up chemical reactions and biochemical recognition of proteins and carbohydrates, rather complex surfaces could be obtained in only few process steps.



**Figure 5. Wetting patterns on microcontact printed SAMs.** Glass substrates are coated with an alkenyl terminated silane SAM and patterned using thiol-ene reactions induced by microcontact printing. Since the molecular ink deposited by microcontact printing is more hydrophilic than the alkenyl SAM, wetting of the patterned surfaces results in selective wetting of the contact area. Data taken from Wendeln CEJ 2012.

Recently, we have also used microcontact printing to pattern polymer brushes grown from surfaces. To this end, a suitable initiator for grafting from polymerization was printed on a pre-made SAM and the growth of polymer brushes only in the contact area was subsequently induced by controlled radical polymerization such as atom transfer radical polymerization (ATRP) or nitroxide mediated polymerization (NMP). In the context of this proposal, the most relevant example is our report on the growth of hydrophilic poly(acrylate) brushes containing azobenzenes as photoswitchable units ([Roling ChemComm 2016](#)). This concept is illustrated in Figure 6. It was observed that co-polymer brushes containing 7.5 % of azobenzene acrylate and 92.5 % of hydroxyethylacrylate can be grown in microscale patterns defined by the PDMS stamp and with a height depending on the polymerization time. To the best of our knowledge, there are no other reports on patterned polymer brushes functionalized with azobenzenes. Moreover, it was found that a water-soluble cyclodextrin polymer can act as a supramolecular glue that leads to strong adhesion between two surfaces functionalized with polymer brushes containing azobenzene due to the formation of multiple host-guest complexes of azobenzenes and cyclodextrins. However, no photoresponsive release was observed, most likely due to a poor photoswitching of the azobenzene in the confinement of the polymer nanofilm between two substrates.





**Figure 6. Photoresponsive polymer brushes containing azobenzenes.** Glass substrates are coated with an alkenyl terminated silane SAM and patterned with an ATRP initiator using click chemistry induced by microcontact printing. Next, co-polymer brushes of azobenzene acrylate and hydroxyethyl acrylate are grown by ATRP exclusively in the contact area. Two substrates functionalized with azobenzene brushes can be glued together using a cyclodextrin polymer as a multivalent supramolecular glue. Data taken from *Röling ChemComm* 2016.

## 1.1 Project-related publications

### 1.1.1 Articles published by outlets with scientific quality assurance.

The following list highlights the most important recent publications from my group regarding photoresponsive supramolecular materials and surface patterning. Publications 1-8 are underlined and discussed in section 1. Publications 9-10 are highly cited papers that demonstrate the impact of our work in this research area.

1. Stricker, L.; Böckmann, M.; Kirse, T.M.; Doltsinis, N.L.; **Ravoo, B.J.** Arylazopyrazole photoswitches in aqueous solution: Substituent effects, photophysical properties and host-guest chemistry. *Chem. Eur. J.* **2018**, 24, 8639–8647.
2. 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.
3. Wiemann, M.; Niebuhr, R.; Ruiz del Valle, A.J.; Cavatorta, E.; **Ravoo, B.J.**; Jonkheijm, P. Photoresponsive bioactive surfaces based on cucurbit[8]uril-mediated host-guest interactions of arylazopyrazoles. *Chem. Eur. J.* **2018**, 24, 813–817.
4. Chu, C.W.; **Ravoo, B.J.** Hierarchical supramolecular hydrogels: Self-assembly by peptides and photo-controlled release via host-guest interaction. *Chem. Commun.* **2017**, 53, 12450–12453.
5. Sagebiel, S.; Stricker, L.; Engel, S.; **Ravoo, B.J.** Self-assembly of colloidal molecules that respond to light and magnetic field. *Chem. Commun.* **2017**, 53, 9296–9299. (Cover image)
6. 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.
7. Röling, O.; Stricker, L.; Voskuhl, J.; Lamping, S.; **Ravoo, B.J.** Supramolecular surface adhesion mediated by azobenzene polymer brushes. *Chem. Commun.* **2016**, 52, 1964–1966.

8. Wendeln, C.; Rinnen, S.; Schulz, C.; Kaufmann, T.; Arlinghaus, H.F.; **Ravoo, B.J.** Rapid preparation of multifunctional surfaces for orthogonal ligation by microcontact chemistry. *Chem. Eur. J.* **2012**, *18*, 5880–5888. (Frontispiece)
9. Nalluri, S.K.M.; Voskuhl, J.; Bultema, J.L.; Boekema, E.J.; **Ravoo, B.J.** Light-responsive capture and release of DNA in a ternary supramolecular complex. *Angew. Chem.* **2011**, *123*, 9921-9925; *Angew. Chem. Int. Ed.* **2011**, *50*, 9747-9751. (cited > 120 times)
10. Wendeln, C.; Rinnen, S.; Schulz, C.; Arlinghaus, H.F.; **Ravoo, B.J.** Photochemical microcontact printing by thiol-ene and thiol-yne click chemistry. *Langmuir* **2010**, *26*, 15966-15971. (cited > 80 times)

## 2 Objectives and work programme

### 2.1 Anticipated total duration of the project

The project is expected to take three years with possibility of renewal.

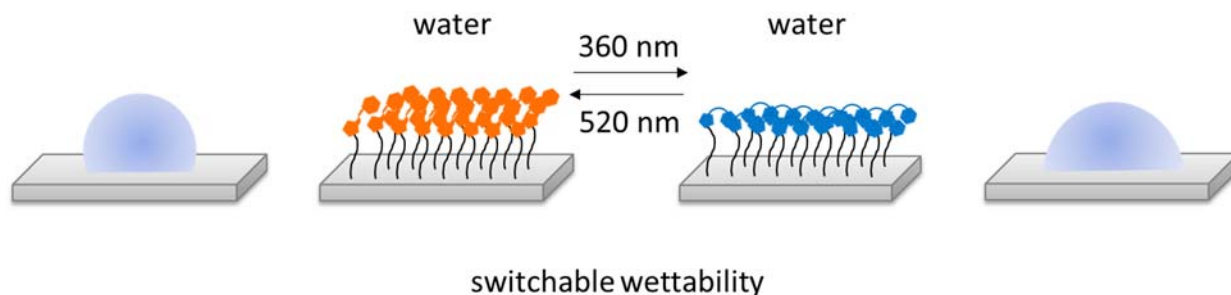
### 2.2 Objectives

This project is motivated by the observation that photoinduced surface wettability can be significantly enhanced using improved molecular photoswitches. The general objective is to investigate the dynamic wetting of surfaces modified with photoresponsive molecular switches of the arylazopyrazole (AAP) structure. On the basis of our preliminary work on AAP photoswitches in aqueous solution, we will now design AAP derivatives that can be immobilized in self-assembled monolayers on substrates such as gold, glass, silicon oxide and aluminium oxide using suitable anchoring groups. The AAP SAMs will also be patterned using microcontact printing and nanoimprint lithography and the dynamic wetting of the resulting photoresponsive surfaces will be investigated. In the second part of the project, the AAPs will be embedded in hydrophilic polymer brushes on glass and silicon oxide so that the effective surface coverage of the photoswitches is significantly higher than in the corresponding SAMs. The polymer brushes will be patterned using microcontact printing and nanoimprint lithography and the dynamic wetting of the resulting photoresponsive polymer surfaces both with water and with particle dispersions will be investigated.

### 2.3 Work programme incl. proposed research methods

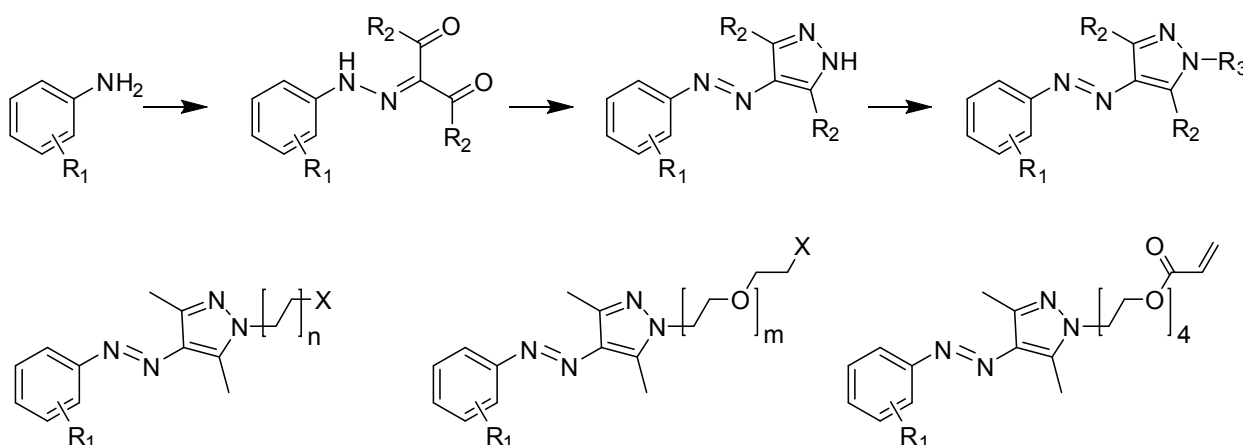
#### 2.3.1 Work package 1: Dynamic wetting of photoresponsive AAP SAMs

In the first work package, we will prepare SAMs of AAPs and investigate the photoresponsive dynamic wetting of the resulting surfaces. Since photoisomerization of the AAP is essentially complete in both directions and the cis-isomer (obtained by UV irradiation at 360 nm) is more polar than the trans-isomer (obtained by green irradiation at 520 nm), it is expected that alternating irradiation results in a switchable wettability of the SAM (Figure 7). We will pursue two strategies to prepare SAMs: (a) in a *direct* approach, we will synthesize AAP derivatives equipped with anchor groups that enable SAM formation; (b) in an *indirect* approach, we will synthesize AAP derivatives equipped with a reactive functional group, so that they can be immobilized on pre-made SAMs using click chemistry. Although the direct method is more straightforward, the indirect method can be advantageous in case the density or quality of the SAM obtained from the direct method is poor and/or the anchor group is not inert towards the functional groups on the AAP and/or the anchor group is poorly compatible with surface patterning.



**Figure 7. Switchable wetting of photoresponsive SAMs of AAP.** Since the *cis*-isomer (obtained by UV irradiation at 360 nm, blue in the cartoon) is more polar than the *trans*-isomer (obtained by green irradiation at 520 nm, orange in the cartoon), it is expected that alternating irradiation results in a switchable wettability of the SAM.

The synthesis of AAP derivatives will follow the established route outlined in the upper part of Figure 8. Starting from aniline (with or without substituents  $R_1$  on the aromatic ring), the azopyrazole is obtained by condensation reactions with a diketone (providing substituents  $R_2$  on the pyrazole ring) and hydrazine. Finally, anchoring group  $R_3$  is introduced by N-alkylation of the pyrazole. In the context of this project,  $R_1$  will either be H or alkyl (for enhanced hydrophobicity) or fluoroalkyl (for superhydrophobicity).  $R_2$  will be methyl for optimal photoswitchability (27). The  $R_3$  group can contain a spacer unit which can be longer or shorter, allowing more or less flexibility of the immobilized AAP, and which can be either hydrophobic (alkyl) or hydrophilic (oligo(ethylene glycol)) resulting in reduced or enhanced wettability of the surface. The anchoring group itself is a thiol (for gold surfaces), a triethoxysilane (for glass and silicon oxide), a phosphonate (for aluminium oxide) or an alkyne (for click chemistry). Thus, using a modular approach, it will be possible to prepare a rather large variety of AAPs that can be immobilized in SAMs. A selection of target molecules is shown in the lower part of Figure 8. It should be emphasized that since we follow mostly well-established and high yield synthesis schemes, the preparation of a large number of AAP derivatives can be achieved in a rather short time so that the synthesis is only a minor and initial phase of the project. Moreover, a lab technician will support this part of the work programme. The structure and purity of the AAP derivatives will be analyzed by NMR spectroscopy, MS and HPLC. The extent, rate and quantum yield for photoisomerization in solution will be investigated using UV-vis and NMR spectroscopy. These data are essential to establish a standard for comparison to the photoisomerization in SAMs.



**Figure 8. Synthesis of AAPs and selection of AAP adsorbates** ( $X = \text{SH}$ ,  $\text{SiOEt}_3$ ,  $\text{PO}_3\text{H}_2$ ,  $\text{C}\equiv\text{CH}$ ,  $n = 2, 4, 6$ ,  $m = 1, 2, 3$ ) and AAP acrylate monomer. The synthesis of AAPs follows a modular approach in which anilines (substituted with  $R_1$ ) are condensed with diketones (substituted with  $R_2$ ) and hydrazine to give the AAP core which is substituted with an anchoring group  $R_3$  by N-alkylation.  $R_3$  includes a hydrophilic or a hydrophobic spacer as well as a surface adsorbate group  $X$ . For the synthesis of polymer brushes,  $R_3$  is terminated with an acrylate.



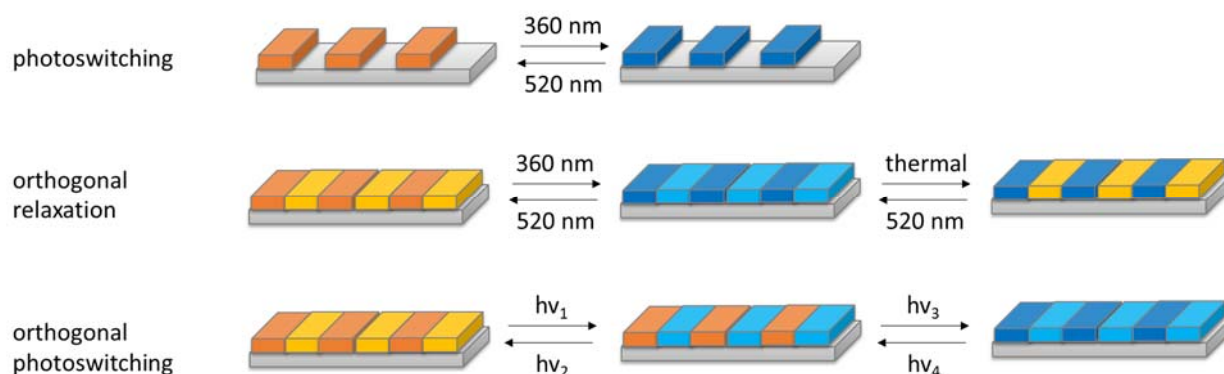
Having a set of AAP adsorbates in hand, we will then proceed to make SAMs on various substrates. SAMs of AAP thiols will be prepared by deposition from solution on gold substrates. Gold substrates are the substrates of choice for SFG and AFM experiments. In addition, both the patterning as well as the preparation of mixed SAMs (see below) is rather straightforward for thiols on gold substrates. SAMs of AAP silanes will be prepared by deposition from solution or alternatively by vapor deposition on glass substrates and oxidized silicon wafers as well as “black” silicon. SAMs of AAP-phosphonates will be obtained by deposition from solution on aluminium oxide ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) substrates. It has been shown that SAMs of alkylphosphonates on aluminum oxide are of very high quality due to the flatness of the substrates and the effective self-assembly process of the monolayer formation (29). Also mixed SAMs of phosphonates can be easily prepared. The quality of the AAP SAMs will be verified using a set of complementary methods such as X-ray photoelectron spectroscopy, IR and SFG spectroscopy (in collaboration with Prof. Björn Braunschweig in Münster). Vibrational SFG is a powerful nonlinear optical tool with inherent interface selectivity and provides information on the molecular structure, composition, and molecular order of interfacial layers (30).

At this stage, we will investigate the photoisomerization of AAP in the SAM. Photoisomerization will be induced by alternating irradiation using UV (360 nm, trans-to-cis isomerization) and green (520 nm, cis-to-trans isomerization) LEDs and will be monitored by IR and SFG spectroscopy. Our first aim will be to establish if indeed AAPs in SAMs display the same photoisomerization in solution and on surface. We anticipate that (similar to azobenzenes, 31) photoisomerization is affected by confinement and reduced degrees of freedom in the molecular monolayer and also by quenching of the photoisomerization by certain substrates, in particular by gold. For this reason, it will be necessary to investigate various combinations of substrates and spacers, so that an optimal combination of monolayer formation and reversible photoisomerization can be achieved. It may also be necessary to “dilute” the AAP SAM with inert adsorbates such as alkylthiols on gold substrates and alkylphosphonates on aluminium substrates since it has often been observed that the photoisomerization of azobenzenes is restricted by confinement and steric hindrance (31).

As soon as we have established optimal conditions for photoswitching, we will investigate the dynamic wetting behavior of the SAMs. Using dynamic water contact angle measurements to determine the advancing and receding contact angles as well as the contact angle hysteresis, we will investigate the dynamic change in surface wettability as a result of photoisomerization. It is our hypothesis that the less polar and more symmetric trans-AAP will form more hydrophobic and less wettable surfaces, whereas the more polar and less symmetric cis-AAP will form more hydrophilic and more wettable surfaces. We will also investigate the correlation of the time-scales of photoisomerization and wetting. Depending on the substitution of the AAP, both the polarity of the trans and cis-isomers may be rather different and also the stability of the cis-isomer as well as the kinetics and the photostationary state of the photoisomerization are likely to be very different. As a result, also the dynamic photoresponsive wetting of the AAP SAMs should show substantial differences depending on the AAP molecular structure and irradiation with UV or green light. Furthermore, we will measure the dynamic wetting of AAP SAMs on nanorough substrates such as black silicon, which may dramatically enhance the absolute changes in wettability (12).

However, we expect even more interesting observations for the dynamic wetting of patterned SAMs of AAPs in which photoswitchable AAPs and photo-inert molecules or two different AAPs are deposited in micro- or even nanoscale patterns (Figure 9). Microscale patterns can be obtained using microcontact printing. In the most straightforward procedure, we will print AAP thiols on gold substrates and AAP phosphonates on aluminium using polydimethylsiloxane (PDMS) stamps with a microscale relief structure. In this way, the AAP SAM is formed only in the contact area, and the remaining surface area can be passivated with a photo-inert adsorbate (alkylthiol or alkylphosphonate). Alternatively, AAP alkyne can likely be printed on a wide range of azide-functionalized substrates (e.g. glass or silicon wafers) and the remaining area can be passivated with a simple alkyne. The resulting patterns will be analyzed using AFM and ToF-SIMS. Using microcontact printing, we will thus obtain AAP SAMs confined in microscale stripes or dots, and we will investigate the dynamic photoresponsive wetting of these patterned surfaces.

In addition, we will print a first AAP and fill the remaining surface area with a second AAP so that a binary micropattern of two AAPs is obtained. By selecting the appropriate combination of AAPs, it will be possible to prepare patterns of AAPs that can be addressed orthogonally (i.e. photoisomerization at different wavelengths) or that relax from cis to trans with very different kinetics (i.e. back-isomerization with different rates) so that in this case rather complex dynamic wetting phenomena can be induced by alternating irradiation at various time scales.



**Figure 9. Patterned surfaces for switchable wettability.** In the simplest case (top panel), one type of AAP is immobilized in a patterned SAM and photoswitched reversibly from trans-AAP (orange) to cis-AAP (blue). Alternatively (middle panel), two AAPs (orange and yellow) are immobilized in a pattern, both are switched from trans to cis (blue and light blue) using irradiation at the same wavelength, but one relaxes from cis to trans significantly faster than the other, so that orthogonal and switchable wettability is obtained. Finally (bottom panel), two AAPs (orange and yellow) are immobilized in a pattern and each can be switched using different wavelengths, so that orthogonal and switchable wettability patterns are obtained.

Our experimental work will be supported by multiscale simulations by PD Dr. Svetlana Gurevich and Prof. Andreas Heuer in Münster. Using a combined approach of molecular dynamics (MD), Monte Carlo (MC) of lattice gas models (LGMs), and density functional theory (DFT) simulations to study the photoswitching of the surfaces at the microscopic level and thin film methods at the mesoscopic level, they will provide an in-depth model of the dynamic wetting of our patterned photoswitchable substrates. Moreover, phase field simulations will be carried out by PD Dr. Rodica Borgia in Cottbus. These simulations will provide insight into the dynamics of a thin liquid film on patterned switchable substrates. In these simulations, the photoisomerization will be modelled as a change in electrical field, reflecting the increased dipole moment of the cis-AAP in comparison to the trans-AAP.

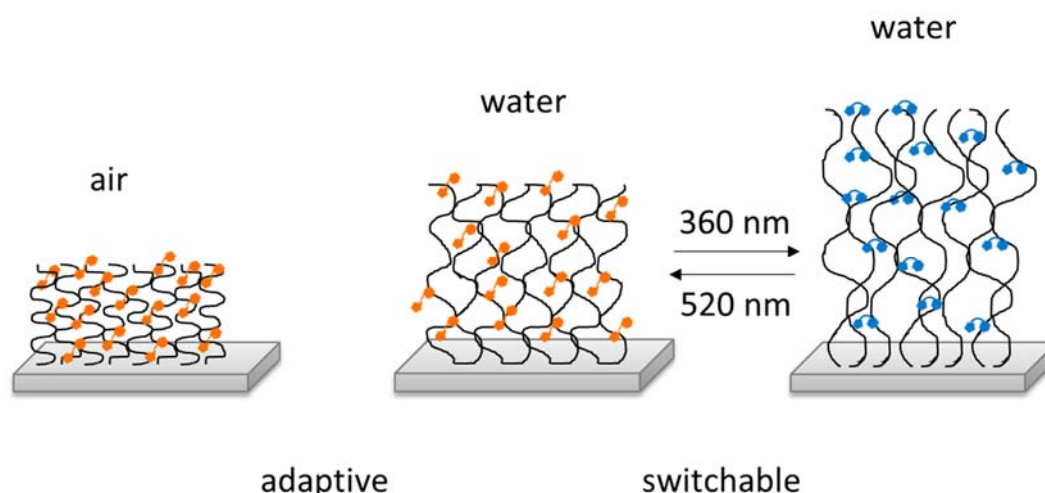
Patterns of AAP SAMs on gold will also be investigated in close collaboration with the group of Prof. Thomas Schimmel and Dr. Stefan Walheim in Karlsruhe, who have previously investigated the phenomenon of photo-tribology as well as the nanomechanical triggering of azobenzene isomerization in SAMs. In the framework of the SPP, we will prepare micropatterns of AAP on ultrasmooth gold substrates (either by microcontact printing or by alternative methods available in Karlsruhe). These patterns will be investigated using AFM. It is expected that photoisomerization leads to a reversible change of the thickness of the SAM (a trans-SAM is normally higher than a cis-SAM) which can be directly measured by so-called “molecular ruler” experiments in AFM. AFM will also be used by the Karlsruhe team to carry out nano-tribological measurements of the photoresponsive SAMs, in the assumption that the trans-AAP and the cis-AAP will show distinctly different friction towards a moving AFM tip. Finally, the patterned AAP SAMs will be highly interesting substrate for the nanomechanical triggering of AAP isomerization. As stated in section 1, cis-AAP is usually less stable than trans-AAP, but thermal relaxation can vary by many orders of magnitude depending on the substituents on the AAP. In our collaboration, we aim to investigate systematically the nanomechanical, AFM tip induced cis-to-trans isomerization of AAPs in SAMs. We will select three AAPs with fast, intermediate and slow relaxation and investigate the nanomechanical isomerization. We hypothesize that the

isomerization in SAMs is a cooperative phenomenon, which depends critically not only on the stability of the isomer but also on the packing and molecular dynamics of the SAMs.

Finally, as an outlook to this part of the project, we aim to make nanopatterned SAMs of AAP using nanoimprint lithography. In this methodology, a sacrificial polymer thin film on a gold substrate is imprinted with a nanostructure and an AAP thiol is subsequently deposited in the imprinted areas. After removal of the polymer layer using a suitable organic solvent, a nanoscale pattern of AAP thiol remains. As for microcontact printing, the interspaces can be filled with an inert thiol or with another AAP thiol. The resulting patterns will be investigated using primarily AFM and IR-NSOM (available at the Center for Soft Nanoscience in Münster). Thus, using nanoimprint lithography we will move from microscale to nanoscale patterned SAMs so that we will be able to investigate dynamic wetting of photoresponsive surfaces also at the nanoscale. Nanoscale patterns will also be of interest for nanomechanical studies (see above), since the cooperative isomerization of AAP likely depends on the domain size that can be addressed.

### 2.3.2 Work package 2: Dynamic wetting of photoresponsive AAP polymer brushes

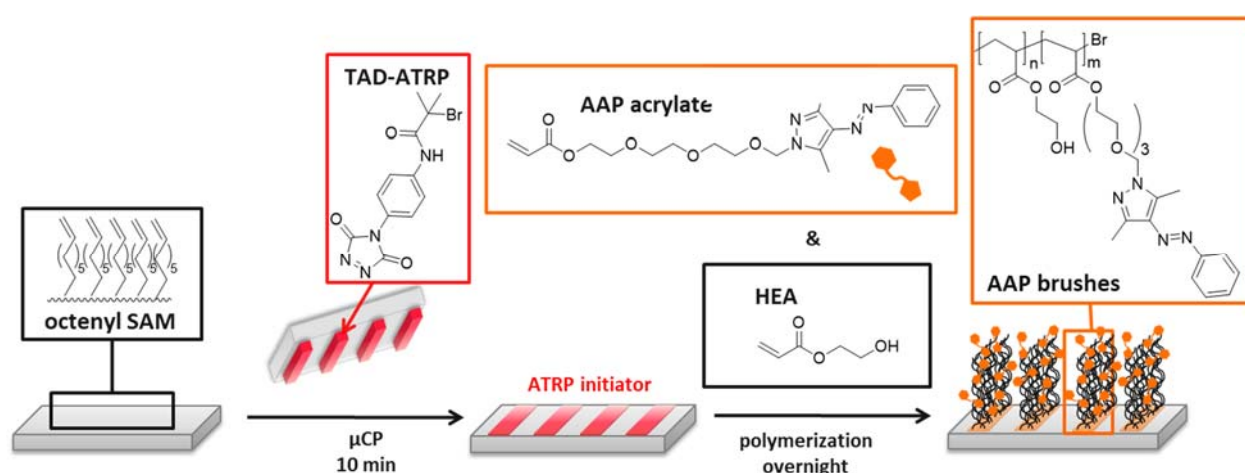
In the second work package, we will investigate the dynamic wetting of hydrophilic polymer brushes containing AAPs. The advantage of polymer brushes versus SAMs is that brushes are more robust, the effective surface coverage of AAP can be much higher (since brushes are quasi-3D), and their polarity can be tuned by selecting an appropriate co-monomer. Moreover, these polymer brushes are expected to show two types of dynamic wetting (32): (a) adaptive wetting as the dry brushes are exposed to water (or another solvent) and (b) photoswitchable wetting as the AAPs in the hydrated brush are photoisomerized (Figure 10). In the latter case, we expect a substantial swelling of the brush layer since the *trans*-AAP is much less hydrophilic than the *cis*-AAP. Photoinduced swelling of azobenzene polymer brushes has been described in the literature, but the observed effect was small due to the low content of azobenzene in the brushes (20). Furthermore, we note that the high density of AAPs in the brushes is particularly attractive to enhance the multivalent binding of micro- and nanoparticles coated with cyclodextrins from aqueous solution. We consider this a specific type of dynamic wetting controlled by photoresponsive supramolecular interactions.



**Figure 10. Adaptive and switchable wetting of photoresponsive polymer brushes containing AAP.** Adaptive wetting occurs when dry polymer brushes are exposed to water (or another solvent) whereas photoswitchable wetting occurs when the AAPs in the hydrated brush are photoisomerized. In the latter case, we expect a substantial swelling of the brush layer since the *trans*-AAP is much less hydrophilic than the *cis*-AAP.

Based on preliminary results using analogous polymer brushes containing functional monomers (Röling ChemComm 2016), we propose to use atom transfer radical polymerization (ATRP) to grow acrylate co-polymer brushes of hydrophilic hydroxyethylacrylate and photoresponsive AAP acrylate. It should be noted that we have previously prepared AAP polymer brushes on silica

microparticles using the same monomers and the same immobilization chemistry (Sagebiel *ChemComm* 2017), so that we are confident that also the preparation of polymer brushes on flat substrates will be successful. The synthesis of AAP acrylate is performed in analogy to the strategy outlined in Figure 8, in which substituent  $R_3$  represents an acrylate terminated oligo(ethylene glycol) which is introduced at the end of the AAP synthesis. We note that the substituents  $R_1$  and  $R_2$  (which determine the photophysical properties of the AAP) can be varied independently of the acrylate anchor  $R_3$ , so that essentially any type of AAP derivative can be (co-)polymerized into the brush. Brushes will be prepared on glass and silicon wafers by immobilization of a suitable ATRP initiator followed by grafting from polymerization from solution. Homogeneous (“full surface coverage”) polymer brushes will be obtained using a commercial silane functionalized ATRP initiator which can be deposited in glass and silicon wafer from solution. Patterned polymer brushes will be obtained using microcontact printing. In that case, the substrate will be coated with a precursor SAM of alkenyl silane, followed by microcontact printing of a triazolinodione (TAD) conjugated ATRP initiator, so that grafting from polymerization is restricted to the micropatterns defined by microcontact printing of the initiator (Figure 11).



**Figure 11. AAP brushes and patterning by microcontact printing.** A clickable initiator for ATRP is printed on an alkenyl terminated SAM on a glass substrate or a silicon wafer. Acrylate brushes are grown by ATRP. The composition and wettability of the brush can be varied by changing the ratio of AAP acrylate and hydroxyethylacrylate. The thickness of the polymer film depends on the length of the polymer brushes, which can be tuned by variation of the polymerization time.

AAP containing polymer brushes will be characterized using X-ray photoelectron spectroscopy, UV-vis and IR spectroscopy and (in the case of patterned brushes) AFM and IR-NSOM. As soon as we have established a reliable polymerization protocol, we will focus on the photoisomerization of the AAP in the brushes. Photoisomerization will be induced using UV (360 nm) and green (520 nm) irradiation and will be monitored using UV-vis spectroscopy of the polymer thin film. Initially, we will investigate the efficiency of the photoisomerization (kinetics and photostationary state) as a function of the layer thickness (i.e. brush length) as well as the density of AAP (i.e. fraction of AAP acrylate vs. hydroxyethylacrylate).

Next, we will focus on the dynamic wetting of the polymer brushes. First, we will investigate the adaptive wetting of the dry polymer brushes using dynamic water contact angle measurements. We expect rather different wetting dynamics depending on the AAP content and the length of the polymer brushes with slower wetting for higher AAP content and longer brushes. Similar to the experiments on AAP SAMs (section 2.3.1), we will then proceed to irradiate the AAP containing brushes in an alternating fashion with UV light and green light and monitor the switchable change in wetting as a result of the photoisomerization using dynamic water contact angle measurements to determine the advancing and receding contact angles as well as the contact angle hysteresis. It is our hypothesis that the trans-AAP brushes are more hydrophobic and less wettable than the cis-AAP brushes. Furthermore, we also expect that the photoresponsive wettability of the brushes will depend on the AAP content of the brushes, since a higher content of AAP will increase the

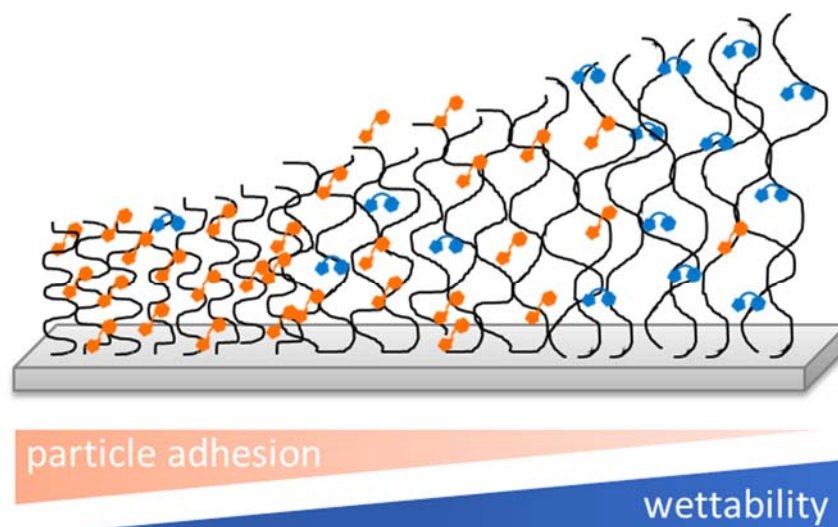
hydrophobicity and reduce the wettability of the brushes. In addition, we expect a significant but reversible swelling of the polymer brushes due to irradiation, since the hydrophilic cis-AAP is likely to be hydrated much more strongly than the hydrophobic trans-AAP. In particular for patterned polymer brushes, photoswitchable swelling should be readily detected using AFM.

As stated in section 1, many AAPs form inclusion complexes with beta-cyclodextrin in aqueous solution. The host-guest chemistry is photoresponsive since the trans-AAP has a much higher affinity for beta-cyclodextrin than the cis-AAP. The high density of AAPs in the brushes is particularly attractive to enhance the multivalent binding of micro- and nanoparticles coated with cyclodextrins from aqueous solution. We consider this a specific type of dynamic wetting controlled by photoresponsive supramolecular interactions. In the framework of this SPP project, we will investigate the dynamic wetting of homogeneous and patterned AAP brushes by cyclodextrin particles. AAP polymer brushes will be prepared as described above. Cyclodextrin coated silica particles will be prepared as described by us in the literature (33) using an efficient two-step immobilization procedure. For easier imaging (see below), the particles can be labelled with a fluorescent dye.

In the case of homogenous ("full surface coverage") brushes, we expect that the multivalent interaction between the AAP in the brush and the cyclodextrin on the particles will depend on the number of individual host-guest complexes that can form between a given particle and the brush modified substrate, so that the overall affinity can be tuned using irradiation with green light (520 nm) to give all-trans-AAP brushes and maximum interaction or UV light (360 nm) to give all-cis-AAP brushes and hence minimal interaction. Under optimal conditions (density of AAP in the brushes, irradiation time, particle size) the interaction of the particles and the surface should be fully reversible. In case the residual interaction with the cis-AAP is still too strong for complete dewetting (i.e. desorption of particles into solution), it can be further reduced by introducing beta-cyclodextrin as a competitive inhibitor in the solution. In initial experiments, we will compare the particle density on the substrate upon green and UV irradiation using *in situ* optical or fluorescence microscopy. Irradiation through a photomask should also provide clear evidence for locally enhanced (green light) or reduced (UV light) wettability. The photoresponsive immobilization of the particles will be investigated in collaboration with Dr. Kirsten Harth in Magdeburg. She will use Frustrated Total Internal Reflection imaging to investigate the dynamic wetting of AAP brushes by cyclodextrin-modified nanoparticles. The imaging system is equipped with laser source suited for photoisomerization in both directions.

In the case of patterned polymer brushes, the pattern will serve as a template for the interaction of the cyclodextrin coated particles with the AAP brushes. In this case we expect highly selective, but photoresponsive wetting of the brushes by the particles, since the particles will bind preferentially to brushes with trans-AAP, very little (if at all) to brushes with cis-AAP, and not at all to the residual areas. The combination of micropatterning and photoresponse opens unique possibilities for the directional wetting and hence photo-controlled movement of particles on the surface. In collaboration with Prof. Alexander Böker in Golm/Potsdam, we will investigate the directed movement of cyclodextrin-modified particles along photoinduced dynamic wettability gradients. Using a sliding photomask or a laser beam, the AAPs in the brushes can be locally photo-isomerized. It is our hypothesis that in this way, cyclodextrin coated particles can be locally displaced from the surface and hence "pushed" out of the UV-irradiated areas or even "pulled" into the green-irradiated areas as a result of preferential local wetting. Furthermore, we propose that also "wettability gradients" can be written into the patterned polymer structures by gradual variation of the irradiation time so that ultimately it may be possible to move particles up and down line patterns (defined by microcontact printing) in a directional fashion (Figure 12). We note that Oh et al have shown that in principle it is possible to induce the motion of liquid droplets on azobenzene surfaces using local irradiation (5). In view of that report, we will also investigate the movement of liquid droplets on the photoinduced wettability gradients. The group of Prof. Alexander Böker in Golm/Potsdam has a microscope that can be used for *in situ* irradiation and imaging of the particles on the polymer brush surface. Phase field simulations of the photoinduced wettability gradients will be carried out by PD Dr. Rodica Borgia in Cottbus.





**Figure 12. Dynamic wetting of photoswitchable gradient brushes.** A homogeneous polymer brush thin film containing AAP units can provide a wettability gradient upon gradient irradiation (longer UV exposure from right to left in the cartoon) since longer irradiation times will result in more extensive photoisomerization from *trans*-AAP (orange) to *cis*-AAP (blue). As a result of adaptive wetting, the brushes will swell more extensively from right to left. However, due to the increasing *trans*-AAP content, cyclodextrin-modified nanoparticles will bind with increasing affinity from left to right. Under optimal conditions, particles as well as liquid droplets may move along the gradient.

Finally, as an outlook to this part of the project, we aim to make nanopatterned polymer brushes containing AAP using nanoimprint lithography. In analogy to the nanopatterning of SAMs described above, a sacrificial polymer thin film on a glass substrate or silicon wafer will be imprinted with a nanostructure and an initiator silane is subsequently deposited in the imprinted areas. ATRP growth of polymer brushes is then induced exclusively in the nanoscale domains of initiator. After removal of the polymer layer using an appropriate solvent, a nanoscale pattern of polymer brushes containing AAP remains. Thus, using nanoimprint lithography we will move from microscale to nanoscale patterned SAMs so that we will be able to investigate dynamic wetting of photoresponsive surfaces also at the nanoscale. Such nanoscale patterns will be of particular interest for the photo-induced directional wetting with particles using host-guest chemistry of AAP and cyclodextrins. It is our hypothesis that the confinement of the AAP in nanoscale line patterns will enhance the collective photo-induced movement of nanoparticles parallel to the pattern.

### 2.3.3 Time schedule

Work packages 1 and 2 have approximately the same work load. We will start with work package 1, involving synthesis of AAP adsorbates (3 months), preparation of SAMs (3 months), dynamic wetting of SAMs (6 months) and dynamic wetting of patterned SAMs (6 months). We will perform the experiments of work package 2 in partial overlap with work package 1, starting with preparation of polymer brushes (3 months), dynamic wetting (6 months) and dynamic wetting with particles (6 months). We reserve 3 months for our input into various collaborations.

## 2.4 Data handling

The data obtained during this project will be published in peer-reviewed journals including extensive supporting information sections providing experimental and analytical details. New compounds will be registered at the CAS and CCDC databases. All original experimental data will be archived for 10 years.

## 2.5 Other information

Not applicable.

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

Not applicable.

## 2.7 Information on scientific and financial involvement of international cooperation partners

No international cooperation is planned.

## 2.8 Information on scientific cooperation within SPP 2171

The priority programme is an excellent opportunity to investigate the dynamic wetting of AAP-modified surfaces. In collaboration with the group of Prof. Björn Braunschweig in Münster, we will perform a detailed spectroscopic analysis (sum frequency generation, SFG) of the photoisomerization in the SAMs. Together, we will also explore the dynamic wetting of the photoresponsive patterned SAMs. In addition, we will collaborate with the group of Prof. Thomas Schimmel and Dr. Stefan Walheim in Karlsruhe to investigate the nanomechanical triggering of the isomerization of the AAP SAMs using local manipulation with an AFM tip. In collaboration with Dr. Kirsten Harth in Magdeburg, we will use frustrated total reflection imaging to investigate the dynamic wetting of AAP brushes by cyclodextrin-modified nanoparticles. In collaboration with Prof. Alexander Böker in Golm/Potsdam, we will investigate the directed movement of cyclodextrin-modified particles along photoinduced dynamic wettability gradients of polymer brushes. Multiscale simulations of the dynamic wetting of our photoswitchable substrates will be performed by Prof. Andreas Heuer and PD Dr. Svetlana Gurevich in Münster and phase field simulations will be performed by PD Dr. Rodica Borcia in Cottbus. Details of these collaborations can be found in the work programme (section 2.3). In addition, we expect numerous small-scale collaborations with other groups in the SPP in which we contribute our expertise in molecular photoswitches, surface modification and surface patterning.

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## 4 Requested modules/funds

### 4.1 Basic Module

#### 4.1.1 Funding for Staff

Funding is requested for 1 PhD student (75% E13) for 36 months. Felix Boisten, who has recently obtained his MSc degree in the Ravoo group in Münster, will make an excellent candidate in view of his MSc thesis on the patterning of functional polyacrylate brushes by microcontact printing. The PhD student will carry out the all experiments described in the work programme.

#### 4.1.2 Direct Project Costs

Funding is requested for consumables, travel expenses and publication costs.

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

Funding is requested for consumables (30.000 Euro in total, i.e. 10.000 Euro per year). Consumables primarily consist of chemicals and solvents required for the synthesis of AAP derivatives, high purity solvents for chromatography and cleaning of substrates, deuterated solvents for NMR, small labware such as vials, syringes, cuvettes, and substrates for SAMs and polymer brushes.

##### 4.1.2.2 Travel Expenses

Funding is requested for travelling (6.000 Euro in total, i.e. 1000 Euro per person per year) so that the PhD student and the principal investigator can attend all SPP events, travel to our collaboration partners and visit one or two conferences.

##### 4.1.2.3 Project-related publication expenses

Funding is requested for publication costs (2250 Euro) such as costs for color figures and/or cover images.

## 5 Project requirements

### 5.1 Employment status information

Bart Jan Ravoo, Prof. Dr.	Professor	permanent	University of Münster
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### 5.2 First-time proposal data

Not applicable.

### 5.3 Composition of the project group

Bart Jan Ravoo, Prof. Dr.	Professor	permanent	University of Münster
Julian Simke MSc	PhD student	non-permanent	University of Münster
Ute Allebrot	Chemical technician	permanent	University of Münster

The principal investigator will plan and supervise the project and write publications. Julian Simke investigates inclusion complexes of AAPs and will contribute to this project through know-how on the synthesis and analysis of AAP derivatives. Ms. Ute Allebrot will assist with the synthesis of AAP derivatives as described in the work programme. On average, she will spend about 10 % of her time on this project.



## **5.4 Cooperation with other researchers**

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

Scientific cooperations within SPP 2171 are outlined in section 2.8 and detailed in the work programme in section 2.3. No other collaborations are planned.

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

Prof. Pol Besenius (University of Mainz), Prof. Alexander Böker (Fraunhofer IAP Golm/Potsdam), Prof. Filip Du Prez (Ghent University, Belgium), Prof. Dong-Sheng Guo (Nankai University, P.R. China), Prof. Rainer Haag (FU Berlin), Prof. Jurriaan Huskens (University of Twente, Netherlands), Prof. Guangtao Li (Tsinghua University, P.R. China), Prof. Peter Schreiner (University of Gießen), Prof. Wilfred van der Wiel (University of Twente, Netherlands).

## **5.5 Scientific equipment**

We have state-of-the-art organic chemistry labs at the Organic Chemistry Institute as well as the Center for Soft Nanoscience (SoN) at the University of Münster. In the Organic Chemistry Institute, we have unlimited access to the analytical facilities (NMR, MS, X-ray) required for the synthesis and analysis of the AAP derivatives. In the Center for Soft Nanoscience, we have access to surface patterning and analysis methods such as (nano)lithography, dynamic contact angle measurements, AFM, ToF-SIMS, XPS and NSOM. In addition, we have IR, UV-vis and fluorescence spectroscopy as well as a Millipore purification system for ultra-pure water available in my group. Thus, we have all instrumentation necessary to carry out this project.

## **5.6 Project-relevant cooperation with commercial enterprises**

Not applicable.

## **5.7 Project-relevant participation in commercial enterprises**

Not applicable.

## **6 Additional information**

The principal investigator declares that no other research project applications regarding this topic are currently funded or considered for funding by the DFG or any other funding agency.