

Project Description – Project Proposals

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Project title:

Dynamic Wetting of Switchable Surface Coatings

Summary

The here proposed switchable surface coatings provide a unique opportunity to dynamically manipulate the surface wettability via external stimuli. Both the surface chemistry and surface morphology (e.g., controlled surface roughness) are responsible for surface wetting properties. To further understand and control the dynamic wetting behavior on material surfaces, we combine the universal switchable surface chemistry (polymers with light responsive spiropyran) with a tailored surface morphology (roughness, structure, patterns, etc.) to generate new light-responsive polymer surface coatings. In collaboration with experimental and theoretical physics groups within the SPP 2171, the physical and chemical processes involved in the switchable surface wettability will be studied in detail.

Project Description**1 State of the art**

Control of the surface wettability of solid substrates has generated great interest both in fundamental research as well as industrial applications.¹⁻⁴ Responsive materials have found extensive uses as controllable surfaces because of their intrinsic reaction to environmental stimuli such as light irradiation, electric fields, heating/cooling, and solvent treatment.⁵ Switchable coatings can dynamically change their surface/interface wetting property upon exposure to an external stimulus. In a recent example of photo-responsive coating surface, Wang et al.³ prepared a nanostructured tungsten oxide films with wettability and photochromic dual-responsive properties by a facile electrochemical deposition process. A reversible wettability conversion between superhydrophobicity and superhydrophilicity was realized by alternating UV irradiation with storage in the dark. The wettability interconversion and photochromism resulted from changes in the redox properties of the metal ions and the number of oxygen vacancies and adsorbed water molecules.⁶ Theoretically, accompanying with the change of surface wettability, the surface tension is also altered correspondingly, which provide a possibility to control the motion of liquids on a responsive surface. Because the surface free energies of flat solid substrates are determined by atomic level constitutions of their outermost surfaces,⁷ the alteration of chemical structures of the outermost monomolecular layers by light (or some other external stimulus) can be used to trigger and manipulate various interfacial phenomena, e.g., wettability.⁸ Thus, if a gradient in surface energy was generated photochemically as a result of spatially controlled changes of chemical structures of an outermost surface, the motion of a liquid can be guided by spatially controlled photoirradiation of the photoresponsive substrate surface on which the liquid is placed. Based on this, Ichimura et al.⁹ successfully realized the macroscopic reversibly motion of liquids on a fat solid surface by photoirradiation of a photoisomerizable monolayer azobenzene coating. When a liquid droplet several millimeters in diameter was placed on azobenzene coating surface, asymmetrical photoirradiation caused a gradient in surface free energy due to the photoisomerization of surface azobenzenes, leading to the directional motion of the droplet (**Figure 1**).

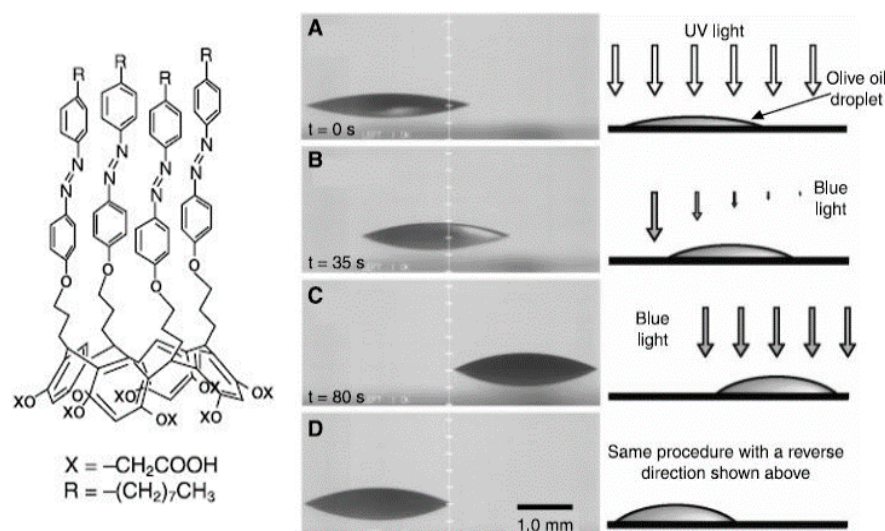


Figure 1. (Left): Schematic diagram of a macrocyclic amphiphile (O-carboxymethylated calix[4]resorcinarene, CRA-CM) tethered to photochromic azobenzene units. (Right) Lateral photographs of light-driven motion of an olive oil droplet on a silica plate modified with. The olive oil droplet on a cis-rich surface moved in a direction of higher surface energy by asymmetrical irradiation with 436 nm light perpendicular to the surface. (A to C) The sessile contact angles were changed from 18° (A) to 25° (C). (D) The moving direction of the droplet was controllable by varying the direction of the photoirradiation. Adapted from reference [9].

For the dynamic surface with reversibly switchable wettability, versatile approaches including appropriate external stimuli¹⁰ and exchange of counterions¹¹ can dynamically trigger the reversible wettability conversion. External stimuli, such as light illumination, temperature, solvents, electrical potential, pH, and others,¹² can change the surface chemical property, conformation and/or morphology of stimuli-sensitive materials, which results in the change of surface wetting behavior. Among various options, light has attracted much attention since it can noninvasively regulate material surface wettability with high spatiotemporal precision.¹³ A variety of photo-responsive inorganic oxides and organic polymers undergo the transition from larger contact angle (CAs) to relatively lower CAs upon ultraviolet (UV) illumination, reverting to the original states with larger CAs after the UV-irradiated films are placed in the dark or exposed to visible (Vis) illumination. This alternating transition can repeat for several cycles under this environment. Several organic materials containing photochromic functional groups, such as azobenzenes, spiropyrans, dipyrindylethylenes, stilbenes, and pyrimidines have the ability to undergo reversible transition of conformation triggered by UV/visible irradiation, leading to changes in their wetting properties.² Among them, spiropyran (SP) is a well-known photochrome for its light-induced reversibly spiropyran-to-merocyanine (SP - MC) isomerization.¹⁴ SP is usually nonpolar and hydrophobic in its closed form. Under UV light irradiation (365 nm), SP dynamically isomerizes to the MC form (open form) and converts into a polar, hydrophilic, and zwitterionic molecule.¹⁵ The hydrophilic/zwitterionic MC isomerizes back to hydrophobic SP after visible light irradiation (550 nm). In this case, the surface wetting property can be dynamically and reversibly switched by the light irradiation with different wavelength and exposure time (**Figure 2**).

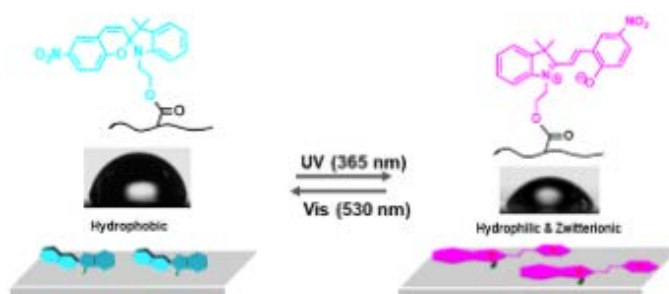


Figure 2. The wetting behavior of the coating surface can be switched based by light induced reversible isomerization of spiropyran from hydrophobic to hydrophilic & zwitterionic.

It is well-known that surface wettability is not only governed by surface chemistry but also the morphology.¹⁶⁻¹⁷ Chemical composition determines the surface free energy, and a lower surface energy leads to higher hydrophobicity. However, the responsive surface wettability of smooth surfaces is usually very limited.² For example, the change in contact angle (CA) is less than 20° on flat surfaces coated with azobenzene.¹⁸ Actually, most surfaces are not flat and show a certain surface roughness and heterogeneity. The basis for all wetting states (substrate-to-air interphase) is Young's equation which describes a thermodynamic equilibrium at the interface between the solid-liquid-air (vapor) phase and is displayed with the static contact angle (CA, θ) for homogeneous, flat surfaces.¹⁹ From a classical point of view, any surface with CA < 90° is hydrophilic and any surface with CA > 90° is hydrophobic. According to current knowledge, the limit should be regarded as the theoretical value of the mathematical model. Recent empirical studies and investigations have shown that a CA of 65° rather than 90° from the theoretical model determines whether a solid material is hydrophilic or hydrophobic.²⁰ This threshold is also called the intrinsic CA.

However, on rough surface, a water droplet can either penetrate or be suspended above the asperities when surface is covered with micro- and/or nanoscale grooves. Wenzel, Cassie, and Baxter extensively studied the wettability effect on surface roughness, which resulted in two models, i.e., the Wenzel model²¹ and Cassie-Baxter (CB)²². In the Wenzel's model, the water droplet will fully penetrate the rough grooves of a textured surface. As a consequence, the effective contact area of a droplet with the surface increases and a roughness factor has to be considered. Wenzel's model predicts that the wetting of hydrophobic surfaces is enhanced by roughness and lessened by roughness for the hydrophilic case. While in the Cassie-Baxter (CB) state, the air pockets trapped inside textured surfaces support the water droplet, suggesting that the fraction of the solid part should be as small as possible for superhydrophobic surfaces. In a word, roughness plays a key role in surface wettability²¹⁻²² and the topological morphology of the material surface is essential to the surface wettability. Therefore, the introduction of surface roughness with switchable surface chemistry has been recognized as a way to enhance or to amplify the responsive wettability of inorganic and organic materials between hydrophilicity and hydrophobicity. However, the dynamic switching of wetting on surfaces, especially rough surface with micro- (or nano-) structures, involves lot of physical processes besides the interfacial switchable chemistry. Herein, we will combine the factors of surface chemistry and surface morphology at the solid-liquid interphase to study the interfacial dynamic wetting behavior. Within the SPP program, we plan to prepare several switchable coating surfaces with different surface structure and surface roughness to study their switchable and dynamical wetting behavior, especially with roughness gradients on surface. The aim of this proposal is to establish a deeper understanding of the physics behind the switching chemistry on the dynamic wettability of switchable surface in collaboration with experimental and theoretical physical groups.

Preliminary work

In the past decade, the development and the fabrication of interfacial material systems with controlled wettability have become some of the most important aspects of surface chemistry.^{4, 23} Although there are several procedures to fabricate controlled wetting surfaces, most of the published protocols have two disadvantages. First, fabricating coatings with special roughness often require a tedious protocol and/or specialized equipment. Second, most of these surface coatings have been prepared on certain substrates and are limited to few materials. Therefore, our group focused on developing novel and substrate-independent methods for constructing controlled wetting surfaces on any kind of substrate by facile approaches. To achieve this goal, we combined several biomimetic approaches, e.g., the adhesive ability of mussel-inspired adhesives, the blood protein adsorptions, and the lotus-like hierarchical structure, to develop universal methods for constructing various controlled wetting systems on any kind of material.

In nature, the adhesion and solidification of a mussel byssus requires only 3-10 min. But a polydopamine (PDA) coating should take several hours to form a thick, dense film.²⁴ The reason for this enormous divergence can be explained by the difference in the precursors with respect to the coating. Polydopamine mimics the chemical functionality of mfp 3 and mfp 5, but neither the molecular weight nor the molecular structure and dopamine content were considered. To overcome these inherent drawbacks of PDA, we recently introduced a mussel-inspired dendritic

polyglycerol (MI-dPG)²⁵⁻²⁶ that mimics not only the functional groups of mfp-1 and mfp-5 but also their molecular weight, molecular structure and the content of catechol groups (**Figure 3**).²⁶ Similar to the mfp protein, the combination of both the catechol and amine moieties is responsible for the strong adhesion on the substrate. Furthermore, the multivalent character of the dendritic polyglycerol scaffold not only exposes most of its functional groups to the periphery (similar to folded proteins) but also significantly accelerates the crosslinking of the polymers during the coating. Under basic conditions, the MI-dPG can undergo covalent crosslinking and form a chemically and mechanically stable coating on virtually all types of materials. Amines can couple with catechols under oxidizing conditions via Michael addition or Schiff base reactions to enhance the crosslinking of the coatings.²⁷ As a result, MI-dPG serves as a remarkable surface coating and can form stable coatings on virtually all types of material surfaces within 10 min or a micrometer-scale coating within hours. Two coating processes are involved during MI-dPG coating. Firstly, the MI-dPG directly adsorbs and anchors onto the substrate and forms a film that constantly thickens with time (similar to PDA coatings). Secondly, MI-dPG starts to crosslink in the solutions and forms partially insoluble particles that will sediment onto the bottom and crosslink with the pre-adsorbed MI-dPG film. The second process has a strong influence on the resulting surface roughness and morphology of the coating. By adjusting the coating parameters, *i.e.*, the coating time, the pH value of buffer solution, concentration of polymer, and the coating depth, we have successfully fabricated multilayer coatings,^{26, 28} highly hierarchical coating,^{25, 28} and gradient coatings.²⁵ The most noteworthy advantage of MI-dPG coating is that the coated layers still contain plenty of reactive -NH₂ groups and the catechol/quinone groups amenable that allows the subsequent attachment of other molecules via imide coupling and the Michael addition or Schiff base reactions. Therefore, superamphiphobic coating surface, switchable coating surface, and biospecific coating surface with excellent bioinert background were easily obtained via post functionalization. In addition to the MI-dPG coating, a similar mussel-inspired polymer coating, the catecholic hyperbranched polyglycerol (hPG-Cat)²⁸⁻²⁹ was also developed as an excellent biofunctional polymer coating on versatile substrates.

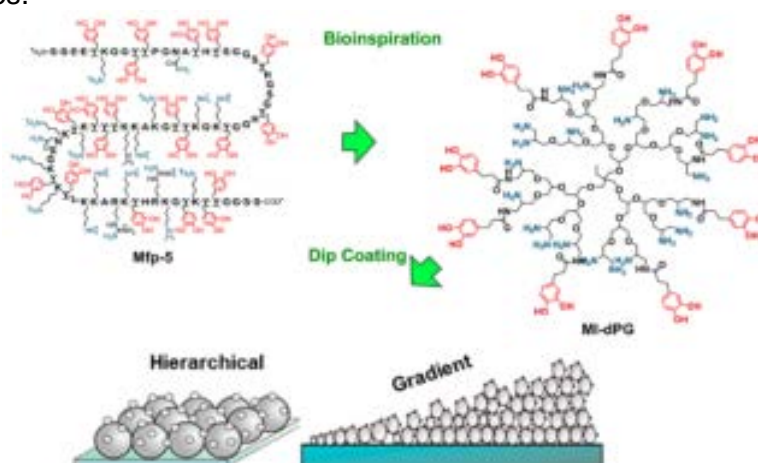


Figure 3. (Top left) Structure of mussel foot protein mfp-5 showing the peptide sequence that contains amine (blue) and catechol (red) units in its side chains. (Top right) chemical structure of mussel-inspired dendritic polyglycerol (MI-dPG). (Bottom) covalent postulated crosslinks of the universal surface coatings (hierarchical coating, and gradient coating).

The thickness and roughness of MI-dPG and other polydopamine coatings are tunable in the range from several nanometers to several micrometers. It is possible to obtain a thin MI-dPG coating and polydopamine coating by tuning several coating parameters, *e.g.*, coating time, polymer concentration, pH value of the buffer, but the problems of homogeneity and stability will come up simultaneously.³⁰ Although the norepinephrine, a dopamine derivative, has been reported to fabricate a relative smooth coating,³¹ it just decreases the size of the aggregates in the coating and is still far from being comparable to monolayer coatings. To extend the catecholic polymer coating from multilayer to highly controllable monolayer, we recently presented for the first time a structurally well-defined universal monolayer coating that are inspired from blood protein adsorption and mussel adhesion (**Figure 4**).³² Blood proteins

spontaneously adsorb on almost all solid material surfaces by denaturing themselves to expose “anchor domains” to the surfaces. Hydrophobic interactions, hydrogen bond formation, ionic or electrostatic attractions, and coordinative interactions are recognized as the main forces causing and driving this adsorption.³³ Proteins, e.g., albumin, adsorb to all surfaces due to their amphiphilic properties. Among them, hydrophobic interactions occur during the adsorption on various solid surfaces.³⁴ Herein, the hydrophobic interaction (mimicry of blood protein adsorption) as well as catecholic anchoring and crosslinking (mimicry of mussel adhesion) were identified as the key factors to promote surface adsorption. A bioinspired amphiphilic block copolymer (PG-CatPh) was therefore designed to integrate these interactions by combining a simple anchoring and efficient crosslinking approach. In this biomimetic amphiphilic block copolymer, the polyglycerol block serves as the hydrophilic domain, while the anchor domain integrates the catechol group, amino group, and the hydrophobic phenyl group. The catechol groups mostly contribute to the coordinative and/or hydrogen bonding on polar surfaces, but also provides hydrophobic domains together with the phenyl groups for anchoring on non-polar surfaces. Besides, just like the hydrophobic amino acids in mfps, especially in mfp-3 “slow” (mfp-3s), the hydrophobic part in the amphiphilic block copolymer will also shield the catechols from the water phase to provide a microenvironment that retards oxidation.³⁵ The amine groups, on the one hand, increase the crosslinking efficiency and, on the other, displace hydrated cations from the mineral surfaces to stabilize the coatings. The ω -N₃ or ω -Br terminal groups are designed to serve as the functional site for secondary modification. The resulting monolayer coatings are highly stable, colorless, only 3-4 nm thick, and can be generated on various planar surfaces and nanosystems. These coatings provide a new platform for material surface modification and can potentially be used in a wide range of applications.

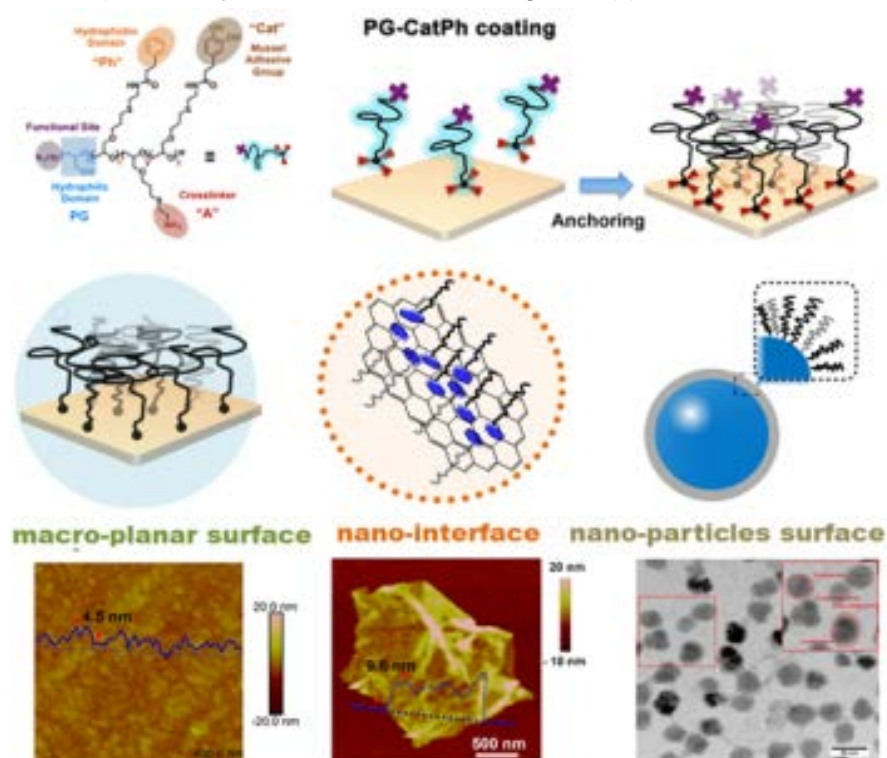


Figure 4. The universal monolayer polymer coating that mimics blood protein adsorption and mussel adhesion. The resulting monolayer coatings are highly stable, colorless, only 3-4 nm thick, and can be generated on various planar surfaces and nanosystems.

In addition to these universal coating technologies, we also successfully immobilized some functional switchable groups onto the coating polymer or synthesized switchable coating polymers to develop several switchable coatings that have outstanding dynamic wetting property (**Figure 5**).³⁶⁻³⁷ The surface wettability of the resulting coating can be dynamically tuned by external stimuli, e.g., light,³⁶⁻³⁷ temperature,³⁸ which are exemplified by the controlled bioorganism-materials interfacial interaction, e.g., protein adsorption, bacterial capture, and cell adhesion.

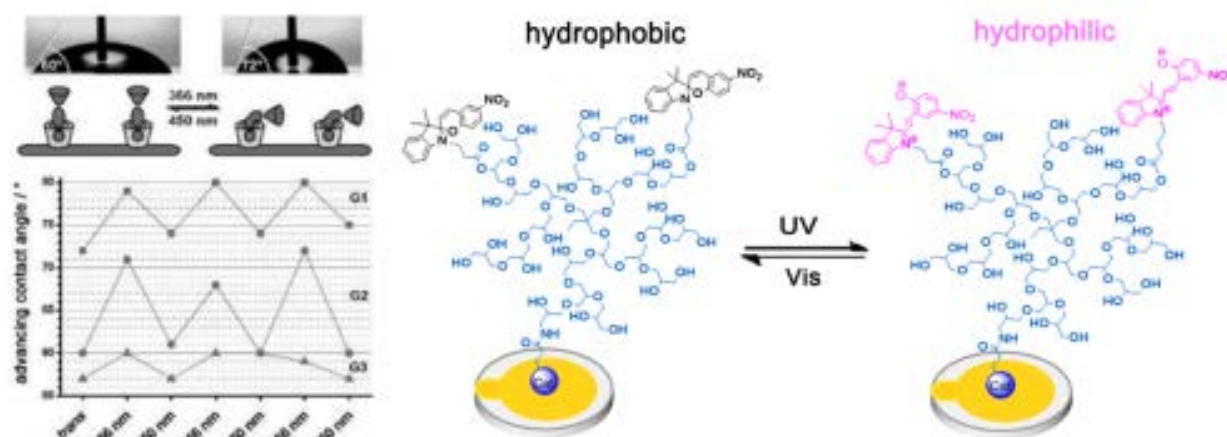


Figure 5. (Left) Switching process of the inclusion complexes G1/2/3-azobenzene-adamantane monitored by contact angle measurements on gold surfaces for three cycles. (Right) The spiropyran moiety on hPG-SP coatings can be photochemically converted between the hydrophobic SP form and hydrophilic zwitterionic MC form.

1.1 Project-related publications

1.1.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

- [1] L. Yu, C. Schlaich, Y. Hou, J. Zhang, P.-L. M. Noeske, R. Haag, Photoregulating Antifouling and Bioadhesion Functional Coating Surface Based on Spiropyran, *Chem. - Eur. J.* **2018**, 24, 7742-7748.
- [2] C. Schlaich, M. Li, C. Cheng, I. S. Donskyi, L. Yu, G. Song, E. Osorio, Q. Wei, R. Haag, Mussel-Inspired Polymer-Based Universal Spray Coating for Surface Modification: Fast Fabrication of Antibacterial and Superhydrophobic Surface Coatings, *Adv. Mater. Interfaces* **2018**, 5, 1701254.
- [3] L. Yu, Y. Hou, C. Cheng, C. Schlaich, P.-L. M. Noeske, Q. Wei, R. Haag, High-antifouling Polymer Brush Coatings on Nonpolar Surfaces via Adsorption-Crosslinking Strategy, *ACS Appl. Mater. Interfaces* **2017**, 9, 44281-44292.
- [4] L. Yu, C. Cheng, Q. Ran, C. Schlaich, P.-L. M. Noeske, W. Li, Q. Wei, R. Haag, Bioinspired Universal Monolayer Coatings by Combining Concepts from Blood Protein Adsorption and Mussel Adhesion, *ACS Appl. Mater. Interfaces* **2017**, 9, 6624-6633.
- [5] C. Schlaich, L. Cuellar Camacho, L. Yu, K. Achazi, Q. Wei, R. Haag, Surface-Independent Hierarchical Coatings with Superamphiphobic Properties, *ACS Appl. Mater. Interfaces* **2016**, 8, 29117-29127.
- [6] C. Schlaich, L. Yu, L. C. Camacho, Q. Wei, R. Haag, Fluorine-free Superwetting Systems: Construction of Environmentally Friendly Superhydrophilic, Superhydrophobic, and Slippery Surfaces on Various Substrates, *Polym. Chem.* **2016**, 7, 7446-7454.
- [7] Q. Wei, K. Achazi, H. Liebe, A. Schulz, P.-L. M. Noeske, I. Grunwald, R. Haag, Mussel-Inspired Dendritic Polymers as Universal Multifunctional Coatings. *Angew. Chem. Int. Ed.* **2014**, 53, 11650-11655.
- [8] Q. Wei, T. Becherer, R.-C. Mutihac, P.-L. M. Noeske, F. Paulus, R. Haag, I. Grunwald, Multivalent Anchoring and Cross-Linking of Mussel-Inspired Antifouling Surface Coatings. *Biomacromolecules* **2014**, 15, 3061-3071.
- [9] Q. Wei, T. Becherer, P.-L. M. Noeske, I. Grunwald, R. Haag, A Universal Approach to Crosslinked Hierarchical Polymer Multilayers as Stable and Highly Effective Antifouling Coatings. *Adv. Mater.* **2014**, 26, 2688-2693.
- [10] O. Nachtigall, C. Kördel, L. H. Urner, and R. Haag, Photoresponsive Switches at Surfaces Based on Supramolecular Functionalization with Azobenzene-oligoglycerol Conjugates, *Angew. Chem. Int. Ed.*, **2014**, 53, 9669-9673.

1.1.2 Other publications

1.1.3 Patents

1.1.3.1 Pending

- [1] L. Yu, Q. Wei, R. Haag, M. Weinhart, Blockcopolymere als bioinerte universelle Monoschichtsysteme, europäische Patentanmeldung 2016, EP 16177279, international Patentanmeldung 2017, PCT / EP 2017/066313, WO 2018/002322 A2

1.1.3.2 Issued

- [2] R. Haag, Q. Wei, I. Grunwald, T. Becherer, M. Weinhart, European patent application 2013, EP2013/184328, Multischicht-Architektur als Antifouling-Beschichtung für vielfältige Substrate.

2 Objectives and work programme

2.1 Anticipated total duration of the project

36 months (01.10.2019-30.09.2022)

2.2 Objectives

The dynamic process of liquids wetting or dewetting on various material surface is ubiquitous in everyday life and is key to many technological applications. The overall goal of this research proposal is to obtain more chemical and physical cues on the dynamic wetting at the solid-liquid interface, providing guidelines in future material surface modifications and polymer coating design. In collaboration with physical and theoretical groups we want to obtain a better understanding of the fundamental dynamic wetting processes (**Figure 6**).

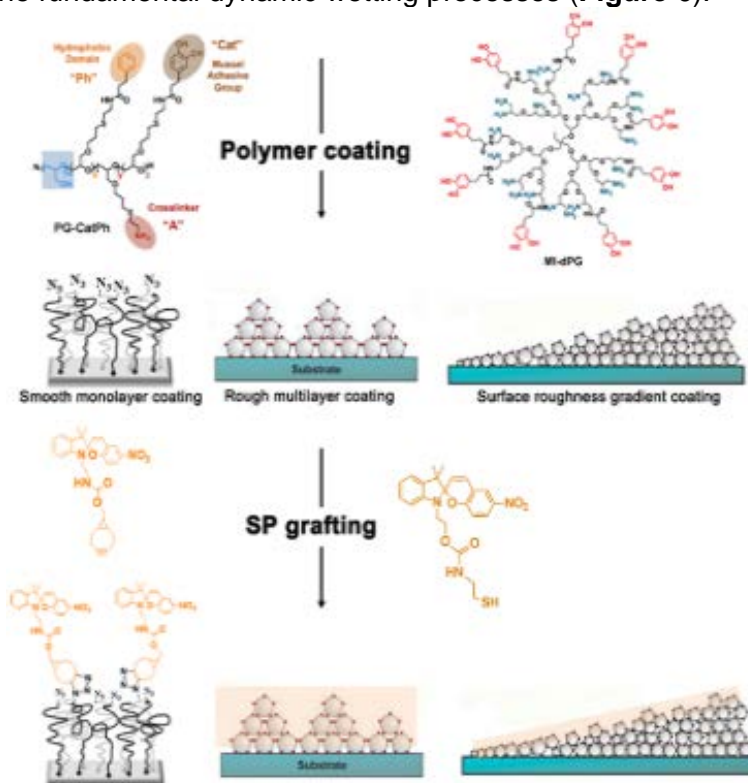


Figure 6. Preparation of smooth monolayer switchable surface coatings, the hierarchical switchable coating surface with high roughness, and the surface roughness gradient switchable coating surface based on our previously reported protocols.

Three kinds of polymer coating with different surface morphologies, i.e., the very smooth monolayer “hairy” coating, the multilayer coating with high roughness and/or hierarchical structure, and the surface roughness gradient coating, will be fabricated. These three coatings will be further modified with light switchable SP molecules (**Figure 6**). This will enable us to dynamically control the wettability and/or liquid droplet moving on the resulting coating surface, to learn the influence of surface geometry on surface wetting behavior, and then further to study the fundamental physics and chemistry behind them in collaboration with experimental (AK Butt, AK Bonn) and theoretical physics groups (AK Stark, AK Thiele).

2.3 Work program incl. proposed research methods

WP1: preparation of the polymer coatings with different surface morphologies and surface roughness.

1. Three polymer coating surface with different surface morphologies and surface roughness will be prepared according to our published methods.

The synthesis of MI-dPG polymer coating was described earlier by our group; dendritic polyglycerol (dPG) is synthesized by a three-step procedure, as described in earlier.³⁹⁻⁴⁰ For the coating and adjustment of surface roughness two strategies can be applied:

1) Hierarchical coating:

Firstly, the MI-dPG microstructured layer is prepared by immersing the respective surface in a MI-dPG solution. Secondly, the MI-dPG nanostructured layer is prepared by immersing the precoated surfaces in a MI-dPG (e.g., 0.5 mg/mL) at pH 7.5.

2) Gradient roughness coating:

The MI-dPG coatings first layer is prepared by immersing the respective surface in a MI-dPG solution. The slide is tilted during the coating as shown in **Figure 7**. For achieving different thickness and/or roughness the process can be repeated.

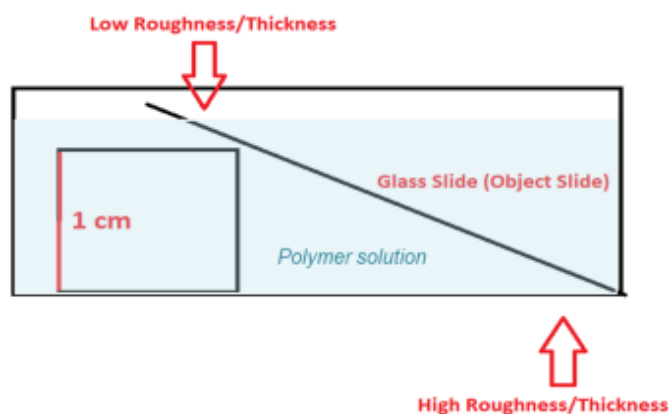


Figure 7. The method to prepared roughness gradient MI-dPG coating.

The PG-CatPh amphiphilic block copolymer was synthesized via the ring-opening anionic polymerization of ethoxyethyl glycidyl ether and allyl glycidyl ether, followed by acetal deprotection, thio-ene amination with cysteamine and Cat/Ph linking by amide formation (see **Figure 4**). The smooth monolayer polymer coating will be prepared at, pH 6. Under acidic conditions, the catechol groups in the block polymer are kept in the catechol state instead of quinone form to prevent the multilayer formation that is caused by the crosslinking and self-polymerization of catechol/quinone groups.

WP 2. The photo-switchable SP molecules will be further immobilized onto the prepared coating surface via click chemistry and Michael reaction.

SP immobilization on hierarchical and roughness gradient MI-dPG coating surface:

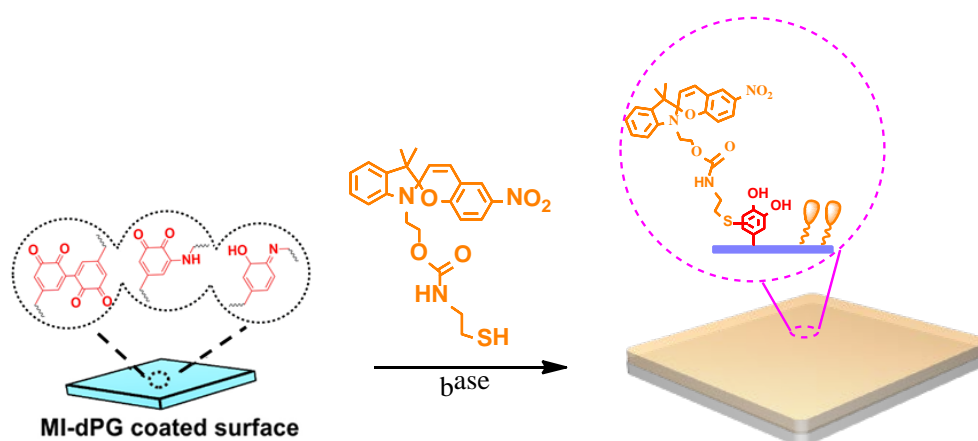


Figure 8. The SP molecules will be grafted onto the hierarchical roughness coating surface and gradient coating surface via the Michael reaction. The SP molecules will be firstly modified with a thiol group and then immobilized onto the corresponding coating surface via the reaction between thiol group and catechol/quinone groups (the Michael reaction).

SP immobilization on a smooth PG-CatPh monolayer surface coating:

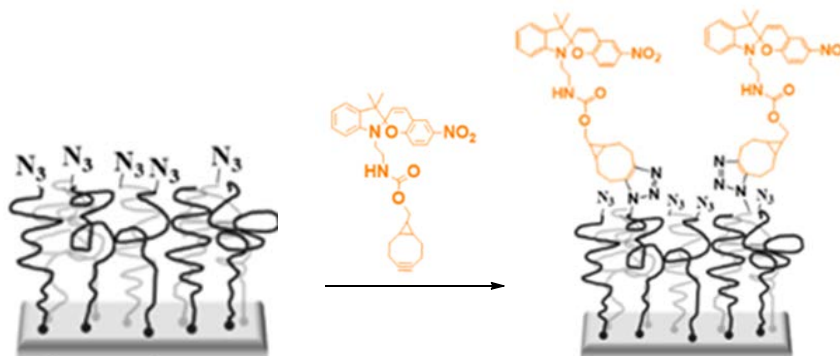


Figure 9. The SP will be modified with cyclooctene and then immobilized onto the prepared smooth monolayer coating surface via the strain-promoted-azide-alkyne-cycloaddition (SPAAC).

WP 3. The surface functionality and the dynamic wetting behavior of the resulting surface coating will be studied in great detail. XPS, FT-IR, AFM, SEM, ellipsometry, etc. will be used to characterize the chemical component, surface morphology, surface roughness, and surface thickness of the resulting switchable coating surface. UV-Vis spectroscopy will be used to study the dynamical isomerization between hydrophobic SP and hydrophilic/zwiterionic MC. The water contact angle testing will be used to study the resulting dynamic wetting behavior under light irradiation. These characterized surfaces will be provided to the collaboration partners at the MPI-P Mainz and the quantitative results of all relevant surface characteristics will be provided to the theoretical modeling group in Berlin.

Cooperations with other groups in the Priority Program

i) H.-J. Butt/R. Berger (MPI-P, Mainz): To measure and analyze the dynamic advancing and receding contact angles of the coated surface we will use the drop adhesion force instrument, which was developed at MPI-PF. The setup allows also to compare the dynamic contact angles before and after light irradiation.

ii) M. Bonn/E. Backus (MPI-P, Mainz): To obtain molecular level information about the polymer and the water structure and dynamics upon photoswitching, static and time resolved Sum Frequency Generation Spectroscopy (SFG) at coated interfaces will be used.

iii) H. Stark (TU Berlin): For the theoretical modelling of water droplets wetting a (photo-) switchable interface, we will provide quantitative data (i.e. thickness, roughness, dynamic contact angle) to the group of Holger Stark and thereby provide an experimental basis for refining the models on the dynamic wetting behavior and of these new interfaces.

iv) U. Thiele (Uni Münster): Also, thin-film gradient dynamics models will be employed to model adaptive substrates. We will provide experimental input for theoretical models of the Thiele group in their limiting case of switchable substrates. Main targets are experiments on wetting dynamics of different liquids on various types of switchable surfaces.

2.4 Data handling

Each laboratory participating in the priority program has the responsibility to store the original data reliably for long-term access. In our research group this is done on local servers, which are daily backed-up by the computer centers. At Freie Universität Berlin, ZEDAT provides such services for data processing and management, which also includes elaborate backup and archiving services, as well as sophisticated recovery procedures. Also, collaboration with the DFG-funded Core Facility BioSupraMol is planned, since they are concerned with extensive data management.

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

2.7 Information on scientific and financial involvement of international cooperation partners

n/a

3 Bibliography

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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

Within this priority program we apply for a PhD position for the period of 36 month (01.10.2019-30.09.2022) according to the salary scale 75% TV-L Berlin.

Funding for	2019		2020		2021		2022	
Staff	Quantity	Sum	Quantity	Sum	Quantity	Sum	Quantity	Sum
PhD student, 75%	1	12,094	1	48,375	1	48,375	1	36,281
Total		12,094		48,375		48,375		36,281
Direct costs	Sum		Sum		Sum		Sum	
small tools, consumables etc.	3,000		12,000		12,000		9,000	
Total	3,000		12,000		12,000		9,000	
Major research instrumentation	Sum		Sum		Sum		Sum	
category:-	-		-		-		-	
Total	-		-		-		-	
Grand total	15,094		60,375		60,375		45,281	

4.1.2 Direct Project Costs

Consumables for financial year 2019

Chemicals, Consumables	EUR	1,125
QCM Chips	EUR	1,500
Special Solvents	EUR	0,375
Sum	EUR	3,000

Consumables for financial year 2020

Chemicals, Consumables	EUR	4,500
QCM Chips	EUR	6,000
Special Solvents	EUR	1,500
Sum	EUR	12,000

Consumables for financial year 2021

Chemicals, Consumables	EUR	4,500
QCM Chips	EUR	6,000
Special Solvents	EUR	1,500
Sum	EUR	12,000

Consumables for financial year 2022

Chemicals, Consumables	EUR	3,375
QCM Chips	EUR	4,500
Special Solvents	EUR	1,125
Sum	EUR	9,000

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

n/a

4.1.2.2 Travel Expenses

We apply for travel money allowing the PI and the employed scientist to attend SPP events.

2020			
	Days	EUR	
SPP workshop (PI)	4	EUR	520
SPP workshop (PhD student)	4	EUR	520
Advanced School (PhD student)	5	EUR	600
Sum		EUR	1640
2021			
	Days	EUR	
SPP workshop (PI)	4	EUR	520
SPP workshop (PhD student)	4	EUR	520
Phd-candidate workshop	4	EUR	520
Sum		EUR	1560
2022			
	Days	EUR	
International conference	5	EUR	2500
Sum		EUR	2500
Total		EUR	5700

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

See central SPP budget.

4.1.2.4 Expenses for Laboratory Animals

n/a

4.1.2.5 Other Costs

n/a

4.1.2.6 Project-related publication expenses

We request 750 € per year for project-related publications to partially cover the costs for color figures and open access.

4.1.3 Instrumentation

4.1.3.1 Equipment exceeding Euro 10,000

n/a

4.1.3.2 Major Instrumentation exceeding Euro 50,000

n/a

4.2 Module Temporary Position for Principle Investigator

n/a

4.3 Module Replacement Funding

n/a

4.4 Module Temporary Clinician Substitute

n/a

4.5 Module Mercator Fellows

n/a

4.6 Module Workshop Funding

See central budget.

4.7 Module Public Relations Funding

See central budget.

5 Project requirements

5.1 Employment status information

For each applicant, state the last name, first name, and employment status (including duration of contract and funding body, if on a fixed-term contract).

Haag, Rainer, Prof. Dr., Institute for Chemistry and Biochemistry, Freie Universität Berlin, permanent position

5.2 First-time proposal data

Only if applicable: Last name, first name of first-time applicant

n/a

5.3 Composition of the project group

The project group will be supported by additional personal that hold permanent positions.
Marlen Selent (technician for separation techniques) 20% E7 permanent
Dr. Carlo Fasting (expert in separation techniques) 10% E13 permanent

5.4 Cooperation with other researchers**5.4.1 Researchers with whom you have agreed to cooperate on this project**

- a) H.-J. Butt/R. Berger (MPI-P, Mainz)
- b) M. Bonn/E. Backus (MPI-P, Mainz)
- c) H. Stark (TU Berlin)
- d) U. Thiele (WWU, Münster)

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

Peter Fratzl (MPI-KG, Golm), Anna Gorbushina (BAM, Berlin), Andreas Lendlein (HZG, Geesthacht/Teltow), Wolfgang Maisson (U. Hamburg), Rolf Mülhaupt (U. Freiburg), Jürgen Rabe (HU Berlin), Bart Ravoo (U. Münster), Peter Seeberger (MPI-KG, Golm), Holger Stephan (Helmholtz-Zentrum Dresden-Rossendorf), Arne Thomas (TU Berlin), Zhibin Guan (Uni California, Irvine) Jay Kitzhakkedathu (UBC Vancouver, Canada), Dusica Maysinger (McGill, Canada), Gerd Multhaupt (McGill Montreal, Canada), Ronit Satchi (Tel Aviv Uni., Israel), Sunil K. Sharma (Delhi University, India), David Weitz (Harvard University, USA), Zhiyuan Zhong (Soochow University, China), Bert Meijer (TUE, The Netherlands), P.-L. M. Noeske (Fraunhofer IFAM, Bremen)

5.5 Scientific equipment

List larger instruments that will be available to you for the project. These may include large computer facilities if computing capacity will be needed.

Our group has access to the core-facility BioSupraMol (for more information see: www.biosupramol.de) where all major instruments are located and kept in service by experienced scientists and technicians. In addition, our group owns and has great experience with a surface IR and QCM with a optical window for the photo-switching experiments.

5.6 Project-relevant cooperation with commercial enterprises

If applicable, please note the EU guidelines on state aid or contact your research institution in this regard.

n/a

5.7 Project-relevant participation in commercial enterprises

Information on connections between the project and the production branch of the enterprise

n/a

6 Additional information

Freie Universität will submit a §91b proposal for an XPS and TOF-SIMS instrument. This equipment will be part of the research building SupraFAB from 2020 and will also be accessible for this project as well as potential collaboration partners within the SPP 2171.