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Reactive Surface Coatings Based on Polysilsesquioxanes: Universal Method toward Light-Responsive Surfaces

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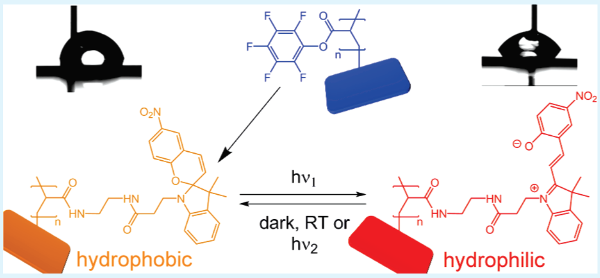
Supporting Information

ABSTRACT: Reactive surface coatings were used as an ideal precursor coating for the fabrication of three different photo-switchable surface coatings in parallel. Different light-responsive moieties, such as azobenzene, salicylideneaniline, and spiropyran, were immobilized on glass, polycarbonate, and steel surfaces. Independent from the underlying substrate, wettability could be switched reversibly by UV irradiation. The maximum switching range was obtained after functionalization of the reactive coating with spiropyran, resulting in a contact angle difference between the two isomeric states of almost 30°.



KEYWORDS: azobenzene, salicylideneaniline, spiropyran, surface wettability, activated ester, light-responsive surface

The surface free energy of flat substrates is mainly determined by spatial arrangement of functional groups on the top-surface region. Hence, the wettability can be fine-tuned by defined adjustment of molecules on top of a surface, for example by means of self-assembled monolayers.[1−4] However, the resulting surfaces are static and can usually not be altered once they have been formed. To prepare adaptable surfaces, different approaches have been presented to realize a switchable wettability by immobilizing various stimuli-responsive moieties onto surfaces.[5−7] A switchable surface wettability was successfully demonstrated taking advantage of stimuli like pH,[8] electrical potentials,[9,10] temperature,[11,12] or light.[13−20]

Such switchable surface coatings have recently received great attention because of the possibility to control fluid flow in micro-channels utilizing systems without any moving parts, which are capable to be scaled down in size to typical microfluidic analysis devices.[21] Especially bioanalytical or bioprocessing devices require certain, mostly very mild conditions. Extreme temperature differences as well as the use of non-aqueous solutions and reactive species have to be avoided. Taking these limitations into account, the use of light as stimuli offers unique opportunities in microfluidic devices. Furthermore, the integration of small light-emitting diodes (LED) into such micro-total analysis systems (μ-TAS) can be realized easily, even in scaled-down devices.[22]

Besides the ability to induce a change in the interfacial properties, the coating material has also to adhere onto the desired substrate. The increased interest in the combination of microfluidics and microarrays has led to the progressive replacement of common inorganic substrates (like glass or silicon) by polymers, especially by polydimethylsiloxane (PDMS)[23,24] or polycarbonate (PC).[25] The adhesion promoter itself, which is used to immobilize a photochemically switchable group onto a surface, must not absorb any light in order not to decrease the photon efficiency of the switching layer.[13] In particular, azobenzene units are the most popular photoresponsive structures, as they show a reversible isomerization even after incorporation into surface coatings. For example, irradiation of azobenzene containing surfactants with UV-light with a wavelength of ~360 nm resulted in changes of the interfacial properties and thus the microdroplet formation on surfaces.[26−28] Azobenzene-containing monolayers on silicon have been prepared and the contact angle (CA) could be decreased by 9° upon irradiation.[29] Light-driven motion of water in glass capillaries coated with azobenzene was demonstrated by Ichimura et al.[15] and they suggested potential application in microscale chemical process systems. A similar approach was taken by Rosario et al.[13], who presented a partial coverage (10−20%) of spiropyran moieties on glass substrates using alkoxy-silanes as adhesion promoters, which yielded in a photo-switchable coating on flat surfaces as well as in glass capillaries. By exposure to UV light, the ring-opening of the spiropyran resulted in a large change of dipole moment due to the formation of the more polar merocyanine isomer.[30] Further, the group of Locklin could prepare photo-switchable polymer brushes by grafting a

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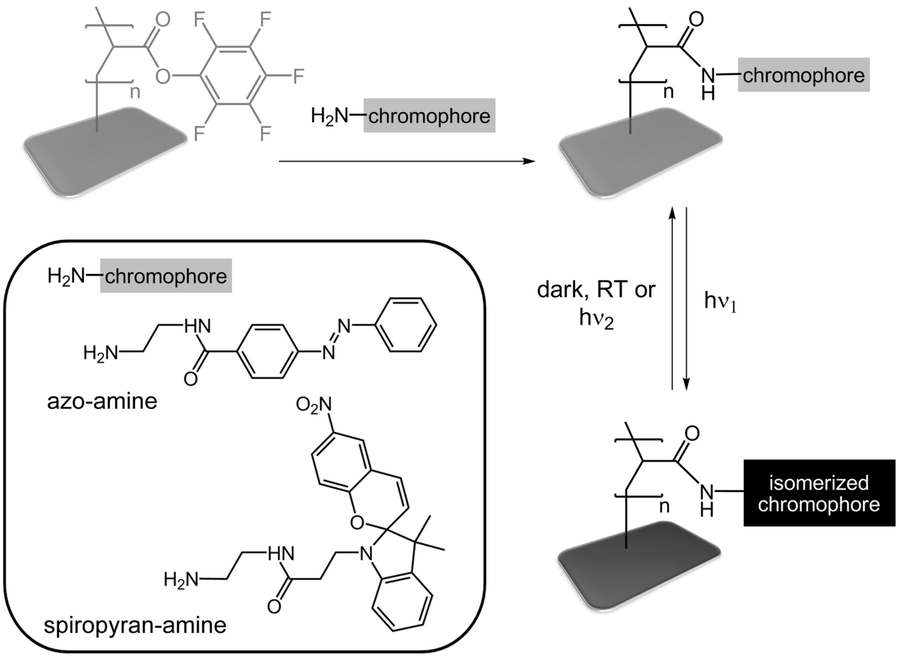
Scheme 1. **Surface-Analogous Reaction to Create Different Photo-Switchable Surface Coatings, Starting from One Reactive Precursor Coating**



spiropyran containing monomer from a surface, which they could even employ for a colorimetric ion sensor.[32]

Most approaches presented in the literature rely on a specific immobilization chemistry in order prepare light-responsive surfaces.[16] Thus, depending on the nature of the substrate the chemistry for the functionalization has to be chosen accordingly. In the present study, we present a different approach based on reactive hybrid polymers that can yield stable and reactive coatings on various substrates. These reactive coatings can then be transformed in a post-modification procedure with different photo-isomerizable amines yielding photo-responsive coatings. Hence, this concept offers the unique possibility to probe different photo-active species and compare their ability to induce a wettability switching on different substrates, which had not been possible previously.

To create reactive surface coatings on different substrates, we spin- or dip-coated poly(methylsilsesqioxane)-poly(pentafluorophenyl acrylate) (PMSSQ-PPFPA) hybrid polymer onto the desired surface. Previous investigations already showed that these hybrid polymers allow the successful formation of very stable and adherent coatings, which are essentially independent from the underlying substrate.[33,34] In the present study, first, PMSSQ-PPFPA (M_n = 32 000 g/mol, M_w/M_n = 1.72) was spin-coated onto three different substrates, glass, steel and polycarbonate (PC), from a 1 wt % solution in THF (4000 rpm, 15 s), resulting in 60 nm thin films.[33] Afterwards, secondary condensation of the PMSSQ part was induced by annealing at 130 °C for 1 h resulting in an irreversible and stable fixation of the layer on the substrate in the same manner as previously reported.[33] Consistent with previous investigations of PMSSQ-based hybrid coatings, it was found that the film prepared on a glass substrate was very smooth as measured by AFM (see the Supporting Information). Next, a functionalization of the surface was performed by a surface-analogous conversion of the activated ester moieties,[35] which was achieved by dipping the reactively coated substrate into a solution of a functional amine at room temperature, yielding a surface that expresses the corresponding functional dye.[33,34] Previous studies have shown that this surface-analogous conversion of activated ester moieties results in surface density of functional groups comparable to self-assembled monolayers.[34]

Table 1. **Advancing and Receding Contact Angles (Θ_a/Θ_r (deg)) of Water on Photo-Switchable Surface Coatings on Different Underlying Substrates**[a]

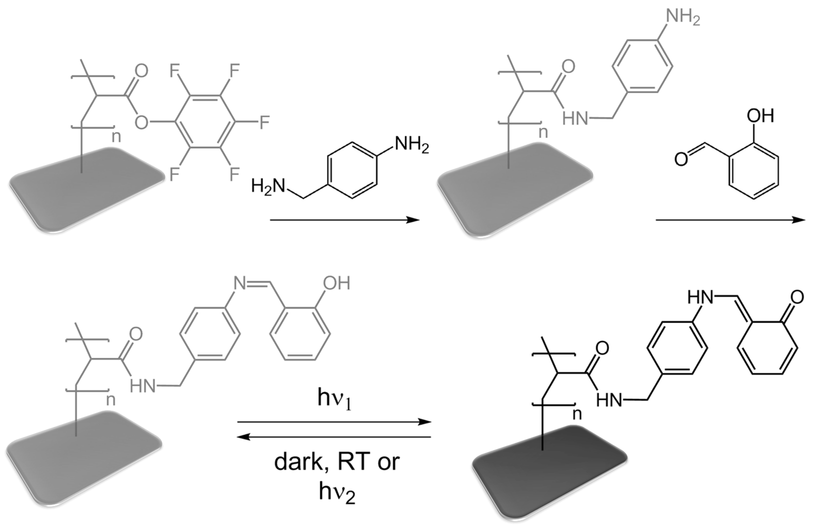
	Θ_a/Θ_r (deg)					
	azobenzene		salicylideneaniline		spiropyran	
substrate	(1)	(2)	(1)	(2)	(1)	(2)
glass	84/78	75/69	70/64	83/78	78/71	48/40
PC	85/78	77/70	72/65	82/78	80/71	52/41
steel	82/76	73/67	70/64	82/79	75/69	46/40

[a] (1) Non-irradiated, (2) after irradiation with λ = 365 nm.

In order to compare the photo-responsive behavior of surface coatings, three different photochromic dyes were investigated, namely azobenzene, salicylidenaniline, and spiropyran. Therefore, amino-functionalized dyes were synthesized. An amine-functionalized azobenzene, *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide [azo-amine], was prepared according to the literature[36]. An amino- functionalized spiropyran was synthesized in two steps starting from 3-(3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indoline]-1′-yl) propanoic acid [SpCOOH] yielding *N*-(2-aminoethyl)-3-(3′,3′-dimethyl-7-nitrospiro[chromene-2,2′-indoline]-1′-yl)propanamide [spiropyran-amine] (see the Supporting Information). The chromophoric salicylidenaniline was prepared directly on the surface, as described below.

As a first example, an azobenzene-based photoactive coating was prepared. The PMSSQ-PPFPA coated substrates were

Scheme 2. Sequential Double Surface-Analogous Reactions to Synthesis Salicylideneaniline Directly on the Surface



dipped into a 10 wt % solution of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide [azo-amine][36] in THF for 1 h (see Scheme 1). Afterwards, the wafers were rinsed twice with ethanol and dried in a nitrogen stream. The advancing and receding contact angles (Θ_a, Θ_r) of water were measured in the dark state as well as after irradiation with UV light for 5 min to induce a trans-to-cis isomerization, which is known to be achieved by irradiation at $\lambda = 365$ nm (see the Supporting Information).[37] On all different substrates, the contact angles decreased after irradiation (see Table 1): (a) on glass, Θ_a was 84° before irradiation and 75° after irradiation ($\Delta\Theta_a = 9°$); (b) on PC, Θ_a was 85° before and 77° after irradiation ($\Delta\Theta_a = 8°$); and (c) on steel, Θ_a was 82° before and 73° after irradiation ($\Delta\Theta_a = 9°$). It is worth noting that the change of wettability, measured by the change of advancing contract angle before and after irradiation, is essentially independent from the underlying material, and that small differences may occur because of different degrees of surface roughness. This switching phenomenon had been repeated at least 10 times to prove the full reversibility (see the Supporting Information). The contact angle difference between the two states of approx. 9° was similar to the values reported for azobenzene monolayers (see reference:[29] $\Delta\Theta_a = 9°$), thereby demonstrating the feasibility of the post-modification procedure for the preparation of photo-responsive surface coatings.

To create a second photo-switchable surface coating starting from the same reactive coating on glass, steel, or PC, we performed a sequence of two surface-analogous reaction steps using 4-aminobenzylamine and salicylaldehyde, similar to a procedure explained elsewhere[38]. During a first conversion step, the coated substrates were dipped into a 10 wt % solution of 4-aminobenzylamine in THF. As shown previously, pentafluorophenyl esters react selectively with aliphatic amines.[35] Thus, the reaction of 4-aminobenzylamine with the PMSSQ-PPFPA coated substrates resulted in the expression of an aromatic amine selectively at the interface. In the second surface-analogous reaction, this aniline functional group was converted with salicylaldehyde by dipping into a 10 wt % THF solution at room temperature, yielding the photo-switchable salicylidenaniline group.[39−41] The salicylideneaniline group is able to isomerize under UV irradiation from the enol-form into the keto-form, which results in a change of color accompanied by a change in the dipole moment.[42−45] The synthetic preparation is shown in Scheme 2. In contrast to azobenzene, irradiation of the salicylidenaniline with $\lambda = 365$ nm[38] for 5 min resulted in an increase of the advancing contact angle on all substrates (see Table 1): (a) on glass, Θ_a was 70° before irradiation and 83° afterwards ($\Delta\Theta_a = 13°$); (b) on PC, Θ_a was 72° before irradiation and 82° afterwards ($\Delta\Theta_a = 10°$); and (c) on steel, Θ_a was 70° before irradiation and 82° afterwards ($\Delta\Theta_a = 12°$). Again, the observed surface characteristics were independent from the underlying substrate. Reversibility as well as repeatability was checked again by performing 10 switching cycles (see the Supporting Information).

The use of spiropyran moieties on surfaces was expected to result in the highest switching range. As already shown before,[13,31,32] spiropyran isomerizes by a ring-opening reaction into a zwitter-ionic merocyanine structure, resulting in a strong change of the dipole moment. To immobilize spiropyran groups on the surface, we converted the reactive PMSSQ-PPFPA coating with *N*-(2-aminoethyl)-3-(3′,3′-dimethyl-7-nitrospiro[chromene-2,2′-indoline]-1′-yl)propanamide [spiropyran-amine] (10 wt % in THF for 1 h) (see Scheme 1). The complete conversion of the activated ester moieties was proven by FT-IR spectroscopy and XPS (see the Supporting Information). After irradiation of the spiropyran functionalized coatings with $\lambda = 365$ nm for 5 min, a decrease in the advancing contact angle was observed on all substrates: (a) on glass, Θ_a was 78° before irradiation and 48° afterwards ($\Delta\Theta_a = 30°$); (b) on PC, Θ_a was 80° before irradiation and 52° afterwards ($\Delta\Theta_a = 28°$); and (c) on steel, Θ_a was 75° before irradiation and 46° afterwards ($\Delta\Theta_a = 29°$). Ten switching cycles of 5 minutes of irradiation followed by 12 h in the dark to induce a back-isomerization into the spiro isomer — have been performed and contact angles before and after each step were measured. As shown in Figure 1, the contact angles can reversibly and reproducibly be switched from approximately 78° to 48°. Furthermore, UV−vis spectra before and after irradiation have been recorded, indicating the isomerization of the dye from the colorless spiro isomer to the colored merocyanine isomer. In agreement with the experiments for azobenzene and salicylidenaniline, the wettability switching of the spiropyran

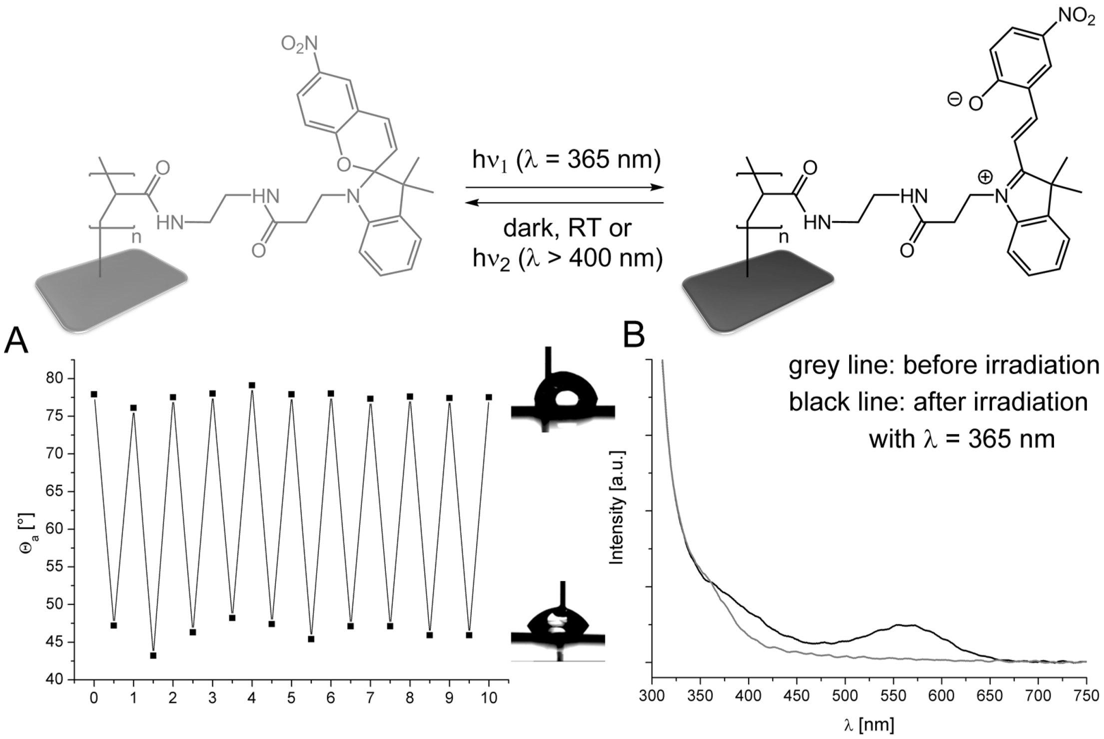


Figure 1. Wettability switching on a spiropyran-functionalized surface. (A) Ten switching cycles between low and high surface wetting (5 min irradiation with $\lambda = 365$ nm; 12 h in dark). (B) UV/vis spectra before and after irradiation of a spiropyran-functionalized coating on glass.

functionalized films is independent from the underlying substrate. However, a larger change of wettability was observed ($\Delta\Theta_a \approx 29°$).

Besides inducing the back-isomerization in the dark for a long time, the back-isomerization could also be induced by irradiation with light of higher wavelength, $\lambda > 400$ nm (see the Supporting Information). On glass the obtained contact angle was 77°, on PC Θ_a was 78° and on steel Θ_a was 74° after irradiation with visible light ($\lambda > 400$ nm) for 5 min (see Table 1). This allows fast switching between a hydrophobic and hydrophilic state.

In contrast to spiropyran containing polymer brushes that were directly grafted from the surface, which resulted only in switching of contact angles smaller than 20°,[31,32] our coating approach seems to provide a better spatial arrangement of the photochromic dyes on the surface. A wettability switching of almost 30° by irradiation with UV light ($\lambda = 365$ nm) or visible light ($\lambda > 400$ nm) is, to the best of our knowledge, the highest light-induced switching of contact angles on smooth, homogenously functionalized coatings. Noteworthy, these light-induced switching of contact angles can be realized on three different substrates, thereby demonstrating the clear advantage of our coating concept. All measured contact angles (Θ_a and Θ_r) are summarized in Table 1. Furthermore, the presented approach is in principle applicable to a wider range of substrates.

In conclusion, the preparation of various photo-switchable surface coatings in parallel could be realized using PMSSQ-PPFPA based reactive surface coatings on three different substrates. This modular approach allows further investigations concerning the effect on the wettability of photo-responsive groups after immobilization on the surface. Furthermore, the photo-isomerization and the resulting effect on the switching behavior in a wetted and non-wetted state may be combined with induced surface roughness, yielding even a higher light-induced switching of contact angles.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental section, synthetic scheme for spiropyran-amine, wettability switching on an azobenzene-functionalized surface and a salicylideneaniline-functionalized surface, AFM-height image of PMSSQ-PFPA coating, FT-IR spectra of spiropyran-amine, PMSSQ-PPFPA coating and after conversion with spiropyran-amine, XPS spectra of the PMSSQ-PPFPA coating before and after conversion with spiropyran-amine, and UV−vis spectra of azobenzene and spiropyran (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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