Chapter 2
Towards Dynamic Control of Wettability by Using Functionalized Altitudinal Molecular Motors on Solid Surfaces

Molecular motors with hydrophobic and hydrophilic functional groups were synthesized and attached to quartz surfaces by interfacial Cu(I)-catalyzed azide-alkyne cycloaddition to achieve dynamic control over the properties of solid surfaces. The functionalized motors preserve their rotary function both in solution and on the surface. The wettability of the surface containing a monolayer of altitudinal motors was shown to depend on whether the motors were assembled in the cis or trans form.

This chapter has been published:
† equal contribution
2.1 Introduction

Modification of surfaces with self-assembled monolayers (SAMs) provides a convenient, flexible, and simple way to create surfaces with tailored properties, including hydrophobicity/hydrophilicity, chirality, catalytic activity, and conductance. Amongst SAM-forming molecules, those that can switch reversibly between two or more states in response to external stimuli such as chemicals, an electric field, or light are of particular interest, since stimuli-responsive molecules are important components for molecular materials and devices. Photoresponsive molecules attract special attention because light hold advantages as a stimulus: it provides a clean and tunable energy input, induce quick responses, enables spatiotemporal control, and can be delivered to a substrate remotely.

Photoresponsive surfaces functionalized with azobenzenes have been studied widely and used to tune surface wettability reversibly using light. The $E \rightarrow Z$ photoisomerization of azobenzenes is accompanied by a change in geometry and dipole moment, which in turn changes the wettability of the monolayers. Due to the inherent changes in dipole moment and molecular structure, azobenzenes can affect the wettability of the monolayer assemblies without an additional functional group being required to ensure sufficient surface wettability change. Nevertheless, additional functional groups and surface pretreatment could enhance the effect of photoisomerization.

Molecular motors based on overcrowded alkenes are a unique class of compounds that can use light to power unidirectional rotary motion. When these molecules are anchored to a surface, two types of rotary motion can be distinguished: azimuthal and altitudinal (Figure 2.1). Molecular motors rotating in an altitudinal orientation are expected to allow for the exposure of the functional group on the rotor to be switched in a cyclic fashion.
Towards Dynamic Control of Wettability By Using Altitudinal Molecular Motors on Solid Surfaces

Figure 2.1 Azimuthal (left) and altitudinal (right) rotary motors. The introduction of functional groups on the fluorene-based rotor is required in order to exploit the rotary motion.

Compared to azobenzenes, altitudinal molecular motors with an non-substituted fluorene as rotor (Figure 2.1, right) are not expected to provide an appreciable change in surface wettability upon rotation that could manifest themselves in a change in macroscopic surface properties. Functional groups have to be introduced to the fluorene-based rotors to develop molecular motor-based interfaces that can undergo cyclic changes in surface wettability.

The interfacial Cu(I)-catalyzed azide-alkyne cycloaddition we reported previously was found to be a reliable method to attach bipodal molecular motors to quartz substrates in an altitudinal orientation.[31,32] In this chapter the synthesis of bipodal molecular motors that contain functional groups at the fluorene-based rotors are described. To test the effect of the functional groups on the rotary motion, photochemical and thermal isomerization studies were carried out in solution. Surface attachment in an altitudinal orientation and the isomerization of surface-bound motors are presented, together with data on the influence of the functional groups on surface wettability.
2.2 Synthesis of bipodal molecular motors

The approach toward the synthesis of motor 2.1 and 2.2, which bears a cyano group and a perfluorobutyl chain on the fluorene-based rotor, is depicted in schemes 2.1, 2.2, and 2.3.

Starting from 2.4, which was prepared by the oxidation of 2-bromofluorene 2.3, fluorenone 2.4 was converted to the corresponding hydrazone 2.5 by heating at reflux in CH₃OH in the presence of hydrazine monohydrate followed by oxidation to the diazo derivative 2.6 with MnO₂ in THF (Scheme 2.1). Thioketone 2.7[31] was reacted with diazo compound 2.6 in a Barton-Kellogg reaction,[33,34] followed by desulfurization, yielding bromo-substituted motor 2.8 in 68% yield over two steps as a mixture of cis/trans isomers.

Scheme 2.1. Synthesis of a bromo-substituted molecular motor.

The cyano group is a relatively hydrophilic substituent and was introduced by means of palladium-catalyzed cyanation[35] of bromo motor 2.8 by using the protocol of Jin and Confalone[36] providing cyano motor 2.9 in 87% yield (scheme 2.2).

Scheme 2.2. Introduction of the cyano and perfluorobutyl substituents to bromo motor 2.8.
A possible way to introduce hydrophobicity into the motor is to functionalize the fluorene-based rotor with a perfluoroalkyl chain. Copper-mediated cross-coupling reactions between aryl halides and perfluoroalkyl iodides have been used successfully to synthesize perfluoroalkylated aryl compounds.\[37,38]\n
By using this approach, coupling bromo motor 2.8 with perfluorobutyl iodide gave compound 2.10 in 73% yield without the evidence of degradation of the motor (scheme 2.2). The next step is to introduce the terminal alkyne groups to the motors that are necessary for surface attachment by means of Cu(I)-catalyzed azide-alkyne cycloaddition. The ester groups in compounds 2.9 and 2.10 were reduced and the corresponding alcohols 2.11 and 2.12 were alkylated with propargyl bromide (Scheme 2.3). The reduction of the ester groups was carried out with LiBH$_4$ in THF. Separation of the two isomers of compound 2.12 was possible at this stage by column chromatography over silica gel (Et$_2$O) to provide cis-2.12 and trans-2.12 in 24 and 34% yield, respectively. Next, the cis/trans mixture of diol 2.11 and the two isomers of diol 2.12 were alkylated with propargyl bromide in the presence of NaH in THF. The cis and trans isomers of alkene 2.1 were separated by column chromatography over silica by using a toluene/Et$_2$O (20:1) eluent mixture. The cis and trans isomers of compounds 2.1 and 2.2 were obtained in 31%, 47%, 64%, and 78% yields, respectively. The structures of dialkyne 2.1 and cis and trans isomers of diol 2.12 were assigned by comparison of their $^1$H NMR spectra with that of previously reported structurally related molecular motors.\[39,40,41,42,43,44]\n
\[\text{Scheme 2.3} \text{ Introduction of terminal alkynes onto substituted motors 2.9 and 2.10, which enables controlled surface modification by means of interfacial Cu(I)-catalyzed azide-alkyne cycloaddition.}\[41\]

\[\text{\dag} \text{ Dr. Gábor Lodon is acknowledged for the synthesis and characterization of 2.2, 2.10, and 2.12.}\]
2.3 Photochemical and thermal isomerization studies in solution

Verification that 2.1 and 2.2 operate as molecular motors\cite{27} requires photochemical and thermal isomerization studies in solution using low-temperature UV/vis absorption and $^1$H NMR spectroscopy.

The UV/vis absorption spectra of a sample of the stable-cis 2.1 and stable-trans 2.1 in CH$_3$OH at 253 K show absorption bands centered at 395 nm (Figure 2.2a and 2.2b, solid lines), whereas under identical conditions the major absorption band of the stable-cis 2.2 and stable-trans 2.2 are centered at 388 nm (Figure 2.3a and 2.3b, solid lines).

![Figure 2.2](image)

Figure 2.2 UV/vis absorption spectra (CH$_3$OH, 253 K) of stable-cis 2.1 (a) and stable-trans 2.1 (b) (solid line). The spectra after UV irradiation (photoisomerization) (dotted line) and heating (thermal isomerization) (dashed line) are also shown; Eyring plot of the conversion of unstable-trans 2.1 to stable-trans 2.1 (a-2), and unstable-cis 2.1 to stable-cis 2.1 (b-2) via thermal isomerization at different temperatures.

Compared to the parent motor without substituents on the rotor part (main absorption band at 378 nm),\cite{31} introduction of the substituents resulted in a slight red-shift of the UV/vis absorption spectrum. Such shifts have already been observed upon the introduction of electron donating or electron withdrawing groups to molecular motors,\cite{35} azobenzenes and stilbenes.\cite{45,46,47} In the case of the
cyano motors 2.1, the maxima of the major absorption band of the stable isomers in CH₃OH are more red-shifted compared to that of the perfluorobutyl motors 2.2. This shift is attributed to the stronger electron-withdrawing character of the cyano group compared to the perfluorobutyl chain.[35]

![Figure 2.3](image-url) UV/vis absorption spectra (CH₃OH, 253 K) of stable-cis 2.2 (a) and stable-trans 2.2 (b) (solid line). The spectra after photoisomerization (dotted line) and thermal isomerization (dashed line) are also shown; Eyring plot of the conversion of unstable-trans 2.2 to stable-trans 2.2 (a-2), and unstable-cis 2.2 to stable-cis 2.2 (b-2) via thermal isomerization at different temperatures.

Irradiation of a sample of stable-cis 2.1, stable-trans 2.1, stable-cis 2.2, and stable-trans 2.2 in CH₃OH at 253 K with UV light (λ_max = 365 nm) led to a red-shift and broadening of their UV/vis absorptions indicating the photochemically induced formation of the unstable isomers (Figure 2.2 and 2.3, dotted lines; Scheme 2.4, steps 1 and 3). The shifted bands are centered at 412 and 407 nm for stable-cis 2.1 and stable-trans 2.1 and 405 and 400 nm for stable-cis 2.2 and stable-trans 2.2, respectively.

During irradiation, clear isosbestic points were maintained in all cases, indicating that the photoisomerization from the stable to unstable form proceeds selectively. Samples were irradiated until no further changes were observed indicating that the photostationary state (PSS) was reached. Allowing the solutions to warm to room temperature (rt) led to reversion to their original absorption
spectra consistent with thermal isomerization to the corresponding stable isomers (Figure 2.2 and 2.3, dashed lines; Scheme 2.4, steps 2 and 4).

**Scheme 2.4** Full 360º rotary cycle for molecular motor 2.1 and 2.2 (R = CH₂CH₂OCH₂CCH).

The activation parameters of the thermal isomerization from unstable-trans 2.1 to stable-trans 2.1 and unstable-cis 2.1 to stable-cis 2.1 (Scheme 2.4, left, steps 2 and 4) were determined at four temperatures (253, 258, 263 and 268 K) in CH₃OH. The thermal isomerization was followed by monitoring the change in absorbance at 450 nm as a function of time. Using the Eyring equation (Figure 2.2a-2 and b-2), it was determined that the thermal isomerization have a Gibbs free energy of activation ($\Delta^\ddagger G^\circ$) of 82.5 kJ/mol (unstable-trans 2.1 → stable-trans 2.1) and 82.2 kJ/mol (unstable-cis 2.1 → stable-cis 2.1). These values correspond to half-lives ($t_{1/2}$) at rt of 57 and 50 s, respectively.

Using the same procedure, the conversion of unstable-trans 2.2 to stable-trans 2.2 and unstable-cis 2.2 to stable-cis 2.2 were monitored at 440 nm as a function of time between 253 K and 273 K (Scheme 2.4, right, steps 2 and 4). The $\Delta^\ddagger G^\circ$ was calculated to be 84.0 kJ/mol (unstable-trans 2.2 → stable-trans 2.2) and 83.3 kJ/mol (unstable-cis 2.2 → stable-cis 2.2) for the thermal isomerization steps. By extrapolation of the plot (Figure 2.3a-2 and b-2), half-lives of 102 s and 81 s at rt were calculated for the unstable-trans 2.2 → stable-trans 2.2 and unstable-cis 2.2 → stable-cis 2.2, respectively.

The values of these half-lives are similar to those obtained for structurally related motors,⁴¹,⁴²,⁴³ indicating that the introduction of the cyano group and
perfluorobutyl chain does not have a significant influence on the thermal isomerization steps.

Further characterization of the unstable isomers and determination of the composition of the PSS was carried out using low-temperature $^1$H NMR spectroscopy for cis and trans isomers of 2.1 and 2.2 in their stable forms (Figure 2.4 and 2.5, a and d; see experimental sections for peak assignments). Irradiation ($\lambda_{\text{max}} = 365$ nm) of a sample of cis or trans isomers of 2.1 and 2.2, in their stable forms, in CD$_2$Cl$_2$ at 218 K resulted in the appearance of new signals in their $^1$H NMR spectra. The identity of the unstable isomers was evident from the downfield shifts of proton Ha, Hb, and Hc (Figure 2.4 and 2.5, a → b and d → e). These downfield shifts of the doublet of the stereogenic methyl groups (proton Ha) of the motors in their stable forms are consistent with the conformational change of the stereogenic methyl substituents from the preferred pseudoaxial [(CH$_3$)$_3$ax] to the disfavored pseudoequatorial [(CH$_3$)$_3$eq] orientation upon photoisomerization (Scheme 2.4, steps 1 and 3). The relative integration of the signals of the stable and unstable isomers revealed similar PSS compositions for all compounds, with slightly less favorable values for alkenes 2.2 (Table 2.1).

<table>
<thead>
<tr>
<th>Molecular Motor</th>
<th>PSS$_{365 \text{ nm}}$ stable/unstable</th>
<th>$^1$H NMR $\delta$ of (CH$_3$)$_3$ax → (CH$_3$)$_3$eq [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis 2.1</td>
<td>1:5</td>
<td>1.28 → 1.42</td>
</tr>
<tr>
<td>trans 2.1</td>
<td>1:3.5</td>
<td>1.29 → 1.45</td>
</tr>
<tr>
<td>cis 2.2</td>
<td>1:2.5</td>
<td>1.29 → 1.41</td>
</tr>
<tr>
<td>trans 2.2</td>
<td>1:2</td>
<td>1.29 → 1.46</td>
</tr>
</tbody>
</table>

When the samples that contained the PSS mixtures (Figure 2.4 and 2.5, b and e) were allowed to warm to rt for 30 min, the $^1$H NMR spectra showed quantitative conversion of the unstable isomers to their corresponding stable isomers (Figure 2.4 and 2.5, b → c and e → f; Scheme 2.4, steps 2 and 4).

$^1$ A possible explanation for this observation is the sensitivity of the photochemical equilibrium to the combination of the substituent and solvent that has already been observed for similar molecular motors. However, for definitive conclusions on the precise solvent effect further studies on the solvent dependence of the PSS composition of alkenes 2.2 should be performed.
Figure 2.4 Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 218 K) of 2.1 (a) stable-cis 2.1 (b) unstable-trans 2.1 formed upon UV irradiation to PSS (c) stable-trans 2.1 obtained after thermal isomerization of unstable-trans 2.1 at rt; (d) stable-trans 2.1 (e) unstable-cis 2.1 formed upon UV irradiation to PSS (f) stable-cis 2.1 obtained after thermal isomerization of unstable-cis 2.1 at rt. Signal assignments are given (R = CH$_2$CH$_2$OCH$_2$CCH).
Figure 2.5 Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 218 K) of 2.2 (a) stable-cis 2.2 (b) unstable-trans 2.2 formed upon UV irradiation to PSS ($\lambda_{\text{max}}$ = 365 nm) (c) stable-trans 2.2 obtained after thermal isomerization of unstable-trans 2.2 at rt; (d) stable-trans 2.2 (e) unstable-cis 2.2 formed upon UV irradiation to PSS (f) stable-cis 2.2 obtained after thermal isomerization of unstable-cis 2.2 at rt. Signal assignments are given (R = CH$_2$CH$_2$OCH$_2$CCH).
By studying the photochemical and thermal behavior of 2.1 and 2.2 in solution using a combination of UV/vis absorption and $^1$H NMR spectroscopy, and by analogy with similar motor systems reported previously, it is concluded that 2.1 and 2.2 function as light-driven rotary motors in solution. In summary, the introduction of the cyano and perfluorobutyl group on the motor moiety does not have a significant influence on the photochemical and thermal behavior of the motors.

### 2.4 Surface attachment and characterization

Molecular motors 2.1 and 2.2 were attached to quartz surfaces through interfacial Cu(I)-catalyzed azide-alkyne cycloaddition\,[48,49] as previously developed for molecular motors with a nonfunctionalized rotor part (Figure 2.1, right).\,[31,32] It was expected that the functional groups would not interfere with the Cu(I)-catalyzed coupling reaction and that the functionalized motors would bind to quartz under identical conditions to those reported previously.\,[31,32] To attach the alkyne-terminated motors 2.1 and 2.2 to quartz surfaces through interfacial Cu(I)-catalyzed azide-alkyne cycloaddition, an azide-terminated monolayer (2.13 SAM) was prepared using azide 2.13 (Scheme 2.5). Piranha-cleaned quartz slides were immersed in a solution of azide 2.13 in cyclohexane/THF that contained a small amount of water and acid to hydrolyze the methoxysilane groups to silanol groups (for further details on surface preparation, see experimental section). Quartz slides were immersed in this hydrolysis solution for 12 h, then rinsed by sonication in toluene, DMF, and CH$_3$OH, and dried under a stream of argon. The water contact angles (WCA) for 2.13 SAM prepared by this method were 83 ± 2°, which is in agreement with contact angles reported earlier for azide-functionalized surfaces.\,[31,32,50,51,52]

To test the effect of the substituents on the photochemical and wetting properties of the modified surface, both isomers of motors 2.1 and 2.2 were attached to quartz substrates functionalized with azide (Scheme 2.5).
Scheme 2.5 Assembly of an azide-terminated monolayer on quartz surface (left). Attachment of the cis and trans isomers of motors 2.1 and 2.2 to 2.13 SAM through a Cu(I)-catalyzed azide-alkyne cycloaddition (right).

The UV/vis spectra of the quartz substrates immersed in a solution of cis and trans isomers of motors 2.1 and 2.2 in DMF (1 mM) in the presence of Cu(I) catalyst showed the characteristic absorption of the motors, which indicates that the attachment was successful (Figure 2.6, solid line, for further details on surface preparations, see experimental section). The maxima of the major absorption band (centered at 399 nm for 2.1 MS and 390 nm for 2.2 MS) and the absorption profile are similar to that observed in CH₃OH solution (Figure 2.2 and 2.3, solid lines).
Figure 2.6 UV/vis absorption spectra (268 K) of (a) stable-cis 2.1 MS, (b) stable-trans 2.1 MS, (c) stable-cis 2.2 MS, and (d) stable-trans 2.2 MS on quartz (solid lines). All isomers of the motors undergo photochemical isomerization upon UV irradiation ($\lambda_{\text{max}} = 365$ nm, dotted lines) and thermal isomerization upon standing at rt overnight (dashed lines).

Based on the assumption that the molar absorptivity ($\varepsilon$) of 2.1 and 2.2 in solution is the same when they are attached to the surface, the surface coverage could be estimated using the Lambert-Beer Law.\footnote{53} Considering that both sides of the surfaces are functionalized with molecular motors, the surface coverage is estimated to be $3.7 \times 10^{-10}$ mol/cm$^2$ (cis-2.1 MS), $4.0 \times 10^{-10}$ mol/cm$^2$ (trans-2.1 MS), $3.0 \times 10^{-10}$ mol/cm$^2$ (cis-2.2 MS), and $3.9 \times 10^{-10}$ mol/cm$^2$ (trans-2.2 MS) for a single side. These values are consistent with monolayer formation and are in good agreement with similar overcrowded alkene systems assembled on a variety of surfaces reported previously.\footnote{54,55}

Irradiation ($\lambda_{\text{max}} = 365$ nm) of the functionalized slides at 268 K resulted in a moderate shift of the UV/vis absorption (centered at 403 nm for unstable 2.1 MS and 394 nm for unstable 2.2 MS; Figure 2.6, dotted line) similar to that observed in CH$_3$OH (Figure 2.2 and 2.3, dotted lines), thus indicating the formation of the
Towards Dynamic Control of Wettability By Using Altitudinal Molecular Motors on Solid Surfaces

unstable form of the surface-bound motors. Upon leaving the sample overnight at rt, the UV/vis absorption reversed, which is consistent with the thermal isomerization process (Figure 2.6, dashed line).

Figure 2.7 Pictures of water droplets on quartz surfaces modified by functionalized altitudinal molecular motors 2.1 and 2.2.

Contact angle measurements were performed on quartz surfaces modified with cis and trans isomers of motors 2.1 and 2.2 (Figure 2.7). Motor-modified surfaces cis-2.1 MS and trans-2.1 MS showed WCA of 67 ± 1° and 60 ± 1°, respectively. The contact angle for cis-2.1 MS is the same as that obtained for the unsubstituted parent motor on quartz, thus indicating that the cyano group does not change the surface wettability considerably, probably due to its small size and comparable polarity to the hydrophilic ethylene glycol units beneath the motor. In the case of cis-2.2 MS, in which the perfluorobutyl chains are likely hidden from the interface, a WCA of 80 ± 2° was measured. For trans-2.2 MS, in which the perfluorobutyl chains are exposed to the interface, a contact angle of 92 ± 1° was obtained that is due to the hydrophobic character of the perfluoroalkyl chains. The effect of the substituent on the wettability of the surface is evident when compared to the motor with a symmetric rotor part (Figure 2.1, right), for which a water contact angle of 67 ± 1° was measured.[31] The higher contact angle in the case of cis-2.2 MS than the unsubstituted symmetric motor analogue is probably due to the shielding of the more polar ethylene glycol units and triazole moieties beneath the chromophore by the perfluoroalkyl chains. The fluorinated chains decrease the free volume in the interface, thereby minimizing the interactions between water and the
hydrophilic components.

Despite the difference in contact angles of water on the different substrates, preliminary attempts to modify the wettability of the surfaces in situ did not show substantial effects. This could be due to the observed lower photoconversion in the case of monolayers 2.1 MS and 2.2 MS than the motors in solution, as indicated by the smaller redshift of the long-wavelength absorption band in their UV/vis spectra (Figure 2.2 and 2.3 versus Figure 2.6). The lower photoconversion is probably due to the intermolecular interactions between the motors within the monolayer. The increased steric crowding in the interface has already been shown to influence the dynamic behavior of the surface-bound motors by slowing down the thermal isomerization step considerably.[32,54]

2.5 Conclusions

From the experimental data it can be concluded that molecular motors that contain cyano and perfluorobutyl substituents were successfully synthesized and attached in an altitudinal orientation to quartz surfaces by using an interfacial Cu(I)-catalyzed azide-alkyne cycloaddition. Furthermore, it was evident by UV/vis absorption spectroscopy that the rotary function of the motors is preserved while confined at the interface. It has also been shown that the surfaces functionalized with the cis and trans isomers of the substituted motors 2.1 and 2.2 provided different water contact angles depending on the polarity and orientation of the substituents. In the next chapter efforts towards improved switching efficiency of the surface-bound motors and exploiting the surface wettability change will be described.
2.6 Experimental Section

2.6.1 General remarks

Flash column chromatography was performed as described by Still et al.\textsuperscript{56} Chromatography: silica gel, Merck type 9385 230-400 mesh. TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm). Preparative layer chromatography: silica gel, Merck, 1 mm, without a fluorescent indicator. TLC plates were visualized by exposure to ultraviolet light (UV) and/or exposure to ceric ammonium molybdate solution (CAM) or an acidic solution of \textit{p}-anisaldehyde (anisaldehyde) followed by brief heating with a heating gun. Mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Orbitrap XL. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Varian VXR-300, a Varian Mercury Plus, or a Varian Inova 500 operating at 299.97, 399.93, and 499.98 MHz, respectively, for the \textsuperscript{1}H nucleus, and at 75.43, 100.57 and 124.98 MHz for the \textsuperscript{13}C nucleus. Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents (CHCl\textsubscript{3}: δ 7.26; CD\textsubscript{2}Cl\textsubscript{2}: δ 5.32). Chemical shifts for carbon are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl\textsubscript{3}: δ 77.0, CD\textsubscript{2}Cl\textsubscript{2}: δ 54.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant in Hz, and assignment. Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp (λ\textsubscript{max} = 365 nm, ± 30 nm). NMR samples were placed 2-3 cm from the lamp. UV/vis absorption spectra were obtained using Hewlet-Packard HP 8543 diode array or a Jasco V-630 spectrophotometer in a 1 cm quartz cuvette. Water contact angles were measured under ambient conditions on a SCA20 Dataphysics instrument with software version 3.60.2. Equilibrium contact angles were obtained by applying 1.25 µL water droplets on 2.13 SAM, 2.1 MS, and 2.2 MS using the sessile drop method. The contact angle was measured at three different locations on each surface and the results were averaged.
2.6.2 Synthesis of compounds and intermediates

Compound 2.4
Triton B (5 mL, 40 % in CH$_3$OH) was added to a stirred solution of 2-bromo-9H-fluorene 2.3 (10 g, 40 mmol) in pyridine (50 mL), upon which the reaction mixture turned red. Air was bubbled through the reaction mixture via a needle for 10 h. The green solution was poured into 10 % aq. HCl (100 mL) and the precipitate was filtered and recrystallized twice from EtOH yielding 2.4 (7.9 g, 76%) as yellow needles. M.p. 146 – 147 ºC; $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.70 (s, 1H), 7.61 (d, $J = 7.4$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.47 (m, 2H), 7.33 (d, $J = 7.9$ Hz, 1H), 7.31–7.25 (m, 1H); $^{13}$C NMR (APT, 50 MHz, CDCl$_3$) δ 192.6, 143.6, 142.9, 137.0, 135.7, 135.0, 133.6, 129.4, 127.5, 124.6, 122.9, 121.7, 120.4; HRMS (APCI-ion trap) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_7$OBr 258.9753, found 258.9751.

Compound 2.5
To a stirred suspension of 2-bromo-9H-fluoren-9-one 2.4 (3.0 g, 11.0 mmol) in CH$_3$OH (30 mL), hydrazine monohydrate (4 mL) was added and the reaction mixture was heated to reflux for 2 h, turning from yellow to orange. The reaction mixture was poured into water (50 mL) and extracted with CH$_2$Cl$_2$ (2×50 mL). The organic phase was dried (MgSO$_4$) and the solvent was evaporated under reduced pressure to give a pale brown solid. Recrystallization from cyclohexane yielded 2.5 as a mixture of E and Z isomers (2.73 g, 91%) as pale brown needles. M.p. 139 ºC; $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.09 – 8.00 (d, $J = 1.6$ Hz, 1H), 7.86 (m, 2H), 7.78–7.66 (m, 2H), 7.65–7.57 (m, 2H), 7.56 (d, $J = 1.7$ Hz, 1H), 7.54–7.47 (m, 1H), 7.47–7.40 (m, 2H), 7.40–7.28 (m, 3H), 6.50 (s, 2H), 6.42 (s, 2H); $^{13}$C NMR (50 MHz, CDCl$_3$) δ 144.2, 143.7, 140.2, 140.0, 137.5, 137.1, 132.3, 131.6, 131.1, 129.9, 129.7, 128.6, 128.4 , 128.2, 128.0, 125.3, 123.9, 121.7, 121.6, 121.0, 120.83, 120.80, 120.6, 119.6; HRMS (ESI-ion trap) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_9$BrN$_2$ 273.0017, found 273.0022.

Compound 2.6
MnO$_2$ (3.8 g, 44 mmol) was added to a stirred solution of 2.5 (3 g, 11 mmol) in THF (100 mL) upon which the color changed from yellow to red. The resulting suspension was stirred for 5 min and filtered over a plug of SiO$_2$. The solvent was removed under reduced pressure yielding 2.6 as a light red solid (2.9 g, 98%). The product was used in the next reaction step without further purification. M.p.
121 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.60 (s, 1H), 7.52–7.35 (m, 3H), 7.32 (t, $J = 7.4$ Hz, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) δ 134.7, 132.7, 130.5, 130.2, 127.6, 126.7, 124.8, 122.0, 121.0, 120.1, 119.2; HRMS (APCI-ion trap) $m/z$: [M – N$_2$ + H]$^+$ Calcd for C$_{13}$H$_7$BrN$_2$ 242.9851, found 242.9803.

**Compound 2.8**

2-bromodiazofluorenone 2.6 (1.23 g, 4.7 mmol) was added to a solution of thioketone 2.7 (1.64 g, 4.3 mmol) in toluene (30 mL). The mixture was heated up to 55 °C for 3 h. The formation of the episulfide was monitored by $^1$H NMR spectroscopy by following the shift of the aromatic proton of the thioketone from 6.66 ppm to 6.35 and 6.37 ppm ($E/Z$ isomers of the episulfide). After the conversion of the thioketone was complete, PPh$_3$ (1.2 g, 4.7 mmol) was added to the episulfide solution and the mixture was heated for an additional 2 h at 75 °C. The reaction mixture was cooled to rt and concentrated in vacuo. EtOAc (60 mL) was added to the mixture, which resulted in the precipitation of PPh$_3$S as yellow crystals. The precipitate was filtered and the procedure was repeated once more. The solvent was removed under reduced pressure. The product was obtained as a mixture of $E$ and $Z$ isomers (42 : 58) after column chromatography (SiO$_2$, n-hexane : EtOAc = 4 : 1) as a yellow solid (1.6 g, 2.93 mmol, 68 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.30-1.34 (m, 9H major, 9H minor), 2.23 (s, 3H, major), 2.24 (s, 3H, minor), 2.54 (d, $J = 14.7$ Hz, 1H major, 1H minor), 3.29 (dd, $J = 5.8, 14.76$ Hz, 1H major, 1H minor), 4.04-4.15 (m, 1H major, 1H minor), 4.26-4.33 (m, 4H major, 4H minor), 4.67 (d, $J = 15.8$ Hz, 1H major), 4.70 (d, $J = 15.7$ Hz, 1H minor), 4.74 (s, 2H, major), 4.75 (s, 2H, minor), 4.83 (d, $J = 15.7$ Hz, 1H, minor), 4.90 (d, $J = 15.8$ Hz, 1H, major), 6.75 (s, 1H, major), 6.77 (s, 1H, minor), 7.17 (t, $J = 7.6$ Hz, 1H, major), 7.29 (t, $J = 7.5$ Hz, 1H, major), 7.32-7.41 (m, 1H major, 3H minor), 7.45–7.48 (m, 1H major, 1H minor), 7.61 (d, $J = 8.1$ Hz, 1H, minor), 7.66 (d, $J = 8.1$ Hz, 1H, major), 7.71 (d, $J = 7.3$ Hz, 1H, major), 7.76-7.79 (m, 1H, minor), 7.82-7.85 (m, 1H, minor), 7.95 (s, 1H, major); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.1, 14.2, 16.2, 18.8, 18.9, 41.3, 41.4, 44.7, 44.8, 60.9, 61.0, 61.4, 65.8, 65.9, 68.1, 69.3, 69.7, 108.2, 108.4, 119.1, 119.6, 120.2, 120.3, 120.4, 120.7, 123.6, 123.7, 126.4, 126.7, 126.8, 126.9, 127.0, 127.1, 128.1, 128.4, 129.3, 129.4, 131.9, 132.1, 134.0, 134.2, 137.4, 137.9, 138.4, 138.7, 139.2, 139.3, 141.3, 143.5, 143.7, 145.1, 145.6, 151.2, 151.7, 152.8, 152.9, 168.4, 168.5, 169.3, 169.5; HRMS (ESI-ion trap) $m/z$: [M + H]$^+$ Calcd for C$_{32}$H$_{32}$O$_6$Br 591.1377, found 591.1379.
**Compound 2.9**

A solution of \((cis/trans)-2.8\) (546 mg, 1.00 mmol) in N,N-dimethylacetamide (22 mL) was added to a mixture of \(\text{Pd}_2(\text{dba})_3\) (18.5 mg, 0.02 mmol, 2 mol%), dppf (22.3 mg, 0.04 mmol, 4 mol%), Zn powder (13.1 mg, 0.20 mmol, 20 mol%) and \(\text{Zn(CN)}_2\) (235.0 mg, 2.00 mmol, 200 mol%) purged with argon and the mixture was heated at 150 °C for 5 h. The reaction mixture was cooled to rt, diluted with EtOAc (50 mL), and washed with saturated aq \(\text{Na}_2\text{CO}_3\) (60 mL), brine (20 mL), dried (\(\text{Na}_2\text{SO}_4\)) and concentrated in vacuo. Purification by column chromatography (SiO\(_2\), n-hexane : EtOAc = 4 : 1) afforded the product as a mixture of trans and cis isomers (~ 2 : 1) as a yellow solid (479 mg, 0.89 mmol, 89%). *Cis/trans mixture:* 

\(\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 1.29-1.36 (m, 9H major, 9H minor), 2.23 (s, 3H, major), 2.25 (s, 3H, minor), 2.57 (d, \(J = 14.8\) Hz, 1H, minor), 2.58 (d, \(J = 14.8\) Hz, 1H, major), 3.31 (dd, \(J = 5.7, 14.6\) Hz, 1H major, 1H minor), 4.04-4.16 (m, 1H major, 1H minor), 4.26-4.34 (m, 4H major, 4H minor), 4.68 (d, \(J = 15.9\) Hz, 1H, major), 4.75 (s, 2H, major), 4.76 (s, 2H, minor), 4.84 (d, \(J = 3.6\) Hz, 2H, minor), 4.92 (d, \(J = 15.9\) Hz, 1H, major), 6.76 (s, 1H, major), 6.79 (s, 1H, minor), 7.26 (m, 1H, major), 7.35 (dt, \(J = 1.0, 7.5\) Hz, 1H, major), 7.40 (d, \(J = 7.7\) Hz, 1H, major), 7.43-7.47 (m, 2H, minor) 7.57 (dd, \(J = 1.4, 7.9\) Hz, 1H minor), 7.63 (dd, \(J = 1.3, 7.9\) Hz, 1H, major), 7.65 (br s, 1H, minor), 7.80 (d, \(J = 7.3\) Hz, 1H, major) 7.83 (d, \(J = 7.4\) Hz, 1H, minor), 7.85-7.91 (m, 2H, minor) 7.88 (d, \(J = 7.9\) Hz, 1H, major), 8.09 (s, 1H, major); \(\text{C NMR (125 MHz, CDCl}_3\) \(\delta\) 14.1, 14.2, 16.2, 18.9, 19.2, 41.4, 44.9, 45.2, 60.9, 61.0, 61.5, 65.7, 65.9, 69.2, 69.3, 108.2, 108.5, 109.4, 109.5, 119.6, 119.8, 120.0, 120.1, 120.2, 120.6, 123.8, 123.82, 127.0, 127.1, 127.2, 127.3, 127.5, 127.6, 128.4, 128.5, 130.1, 130.4, 132.1, 132.3, 133.6, 133.9, 137.3, 137.7, 137.8, 138.3, 139.5, 140.1, 142.6, 143.3, 143.8, 143.9, 145.1, 145.4, 151.6, 151.8, 154.5, 154.7, 168.4, 169.5, 169.6; HRMS (ESI-ion trap) \(m/z\): \([M + \text{Na}]^+\) Calcd for \(\text{C}_{33}\text{H}_{31}\text{NO}_6\text{Na}\) 560.2044, found 560.2022.

**Compound 2.11**

A solution of \((E/Z)-2.9\) (339 mg, 0.63 mmol) in THF (22 mL) was added to a suspension of \(\text{LiBH}_4\) (14.4 mg, 0.66 mmol) in THF (3 mL) and the mixture was stirred at rt for 90 min. The mixture was diluted with EtOAc (25 mL) and washed with \(\text{H}_2\text{O}\) (20 mL), brine (10 mL), dried (\(\text{Na}_2\text{SO}_4\)) and concentrated in vacuo. Purification by flash column chromatography (SiO\(_2\), EtOAc) afforded \(2.11\) as a mixture of isomers (1 : 1.7) as a yellow solid (152 mg, 0.34 mmol, 55%). \(\text{H NMR (500 MHz, CDCl}_3\) \(\delta\) 1.36 (d, \(J = 6.6\) Hz, 3H, minor), 1.37 (d, \(J = 6.7\) Hz, 3H, major), 2.18 (s, 3H, minor), 2.19 (s, 3H, major), 2.61 (d, \(J = 14.9\) Hz, 1H, minor),
2.62 (d, $J = 14.8$ Hz, 1H, major), 3.34 (dd, $J = 5.70$, 14.8 Hz, 1H, major), 3.92-4.23 (m, 9H, major), 4.28-4.32 (m, 1H, minor) 6.90 (s, 1H, major, 1H minor), 7.22 (t, $J = 7.6$ Hz, 1H, major), 7.33-7.38 (m, 2H, major), 7.41-7.49 (m, 2H, minor), 7.56 (dd, $J = 1.3$, 7.9 Hz, 1H, minor), 7.63-7.65 (m, 1H, major, 1H minor), 8.10 (s, 1H, major); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 155.0, 154.8, 153.4, 153.0, 145.6, 144.6, 144.5, 143.2, 142.8, 140.2, 139.6, 139.6, 139.6, 138.5, 137.8, 137.4, 133.3, 132.8, 140.2, 129.985, 128.6, 128.1, 127.3, 127.3, 127.2, 127.1, 127.0, 123.8, 123.4, 120.7, 120.3, 120.2, 120.1, 119.9, 119.8, 109.6, 109.1, 108.3, 108.1, 74.4, 74.3, 70.6, 70.6, 64.4, 62.2, 62.0, 61.0, 45.0, 44.8, 41.6, 41.5, 19.2, 18.9, 16.1, 15.9; HRMS (ESI-ion trap) $m/z$: [M + Na]$^+$ Calcd for C$_{29}$H$_{27}$NO$_4$Na 476.1832, found 476.1843.

**Compund 2.1**

A solution of (E/Z)-2.11 (160 mg, 0.35 mmol) in THF (14 mL) was added dropwise to the suspension of NaH (95%, 34.45 mg, 1.36 mmol) in THF (6 mL) and the mixture was stirred at rt for 30 min. To this mixture propargyl bromide (80 % in toluene, 170 µL, 1.53 mmol,) was added. The solution was stirred at rt for 12 h. The mixture was diluted with EtOAc (25 mL) and washed with H$_2$O (20 mL), brine (10 mL), dried (Na$_2$SO$_4$) and concentrated 	extit{in vacuo}. Purification by column chromatography (SiO$_2$, n-hexane : EtOAc = 4 : 1) afforded the product as a mixture of E and Z isomers as a yellow solid (118 mg, 0.22 mmol, 63%). 85 mg (0.16 mmol) of the E/Z mixture was separated by column chromatography (SiO$_2$, toluene : Et$_2$O 20 : 1). Stable-cis 2.1 (26 mg, 0.05 mmol, 31%, $R_f$ = 0.45) was obtained as a yellow solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 1.34 (d, $J = 6.7$ Hz, 3H), 2.16 (s, 3H), 2.41 (t, $J = 2.4$ Hz, 1H), 2.49 (t, $J = 2.4$ Hz, 1H), 2.58 (d, $J = 14.8$ Hz, 1H), 3.32 (dd, $J = 5.7$, 14.7 Hz, 1H), 3.92-3.94 (m, 2H), 4.00 (t, $J = 4.77$ Hz, 2H), 4.12 (quin, $J = 8.0$ Hz, 1H), 4.23-4.30 (m, 4H), 4.31-4.32 (m, 4H), 6.88 (s, 1H), 7.40 (dt, $J = 1.1$, 7.4 Hz, 1H), 7.45 (dt, $J = 1.5$, 7.6 Hz, 1H), 7.55 (dd, $J = 1.4$, 7.9 Hz, 1H), 7.65 (d, $J = 0.8$ Hz, 1H), 7.83 (dd, $J = 0.5$, 7.9 Hz, 1H), 7.87 (dd, $J = 0.9$, 7.3 Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.1, 19.0, 41.5, 45.0, 58.4, 58.6, 68.1, 68.2, 69.3, 72.0, 74.4, 74.8, 108.5, 109.2, 119.7, 119.9, 120.7, 123.8, 126.8, 127.2, 128.5, 130.0, 131.8, 132.8, 137.7, 137.9, 140.2, 142.6, 144.0, 146.2, 153.7, 155.5; UV/vis (CH$_3$OH, 253 K): $\lambda_{max}$ (ε) = 395 nm (25299 M$^{-1}$cm$^{-1}$). Stable-trans 2.11 (40 mg, 0.075 mmol, 47%, $R_f$=0.55) was obtained as a yellow solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 1.36 (d, $J = 6.7$ Hz, 3H),
2.18 (s, 3H), 2.43 (t, $J = 2.3$ Hz, 1H), 2.49 (t, $J = 2.3$ Hz, 1H), 2.59 (d, $J = 14.8$ Hz, 1H), 3.32 (dd, $J = 5.9$, 14.8 Hz, 1H), 3.89-3.93 (m, 2H), 3.99 (t, $J = 4.7$ Hz, 2H), 4.03-4.16 (m, 2H), 4.22-4.38 (m, 2H), 6.87 (s, 1H), 7.22 (t, $J = 7.3$ Hz, 1H), 7.33 (t, $J = 7.3$ Hz, 1H), 7.38 (d, $J = 7.9$ Hz, 1H), 7.63 (dd, $J = 0.8$, 7.9 Hz, 1H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 8.09 (s, 1H); 13C NMR (125 MHz, CDCl$_3$) $\delta$ 16.0, 19.3, 41.5, 45.0, 58.3, 58.6, 68.0, 68.2, 69.3, 71.6, 74.6, 74.8, 108.3, 109.5, 120.0, 120.1, 120.3, 123.6, 127.1, 127.2, 128.2, 130.0, 132.1, 133.0, 137.3, 138.6, 143.2, 143.9, 145.8, 153.3, 155.3. 2.1; UV/vis (CH$_3$OH, 253 K): $\lambda_{\text{max}}$ ($\varepsilon$) = 395 nm (22743 M$^{-1}$ cm$^{-1}$). Stable 2.1: HRMS (ACPI-ion trap) m/z: [M + H]$^+$ Calcd for C$_{35}$H$_{31}$NO$_4$ 529.2253, found 530.2324.

2.6.3 Low temperature $^1$H NMR spectroscopic characterization of the unstable isomers of 2.1 and 2.2 and procedure to determine the composition of the photostationary state

Irradiation experiment to generate unstable-trans 2.1

Stable-cis 2.1 (2 mg) was dissolved in CD$_2$Cl$_2$ (1 mL). This sample was placed in an NMR tube and irradiated ($\lambda_{\text{max}} = 365$ nm) at 218 K at a distance of 3 cm from the center of the lamp. $^1$H NMR spectra of the sample were taken before, during and after irradiation at 218 K. No further changes were observed after 7 h of irradiation. The relative integration of the absorptions from the two isomers revealed a PSS ratio 1/5 for stable-cis 2.1/unstable-trans 2.1 (Figure 2.4b). After warming the sample to rt, only the stable isomers were observed by (Figure 2.4c). Stable-cis 2.1 (Figure 2.4a): $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 218 K) $\delta$ 1.28 (d, $J = 6.5$ Hz, 3H), 2.08 (s, 3H), 2.51 (s, 1H), 2.56-2.60 (m, 2H), 3.28 (dd, $J = 5.4$, 14.7 Hz, 1H), 3.80-3.88 (m, 2H), 3.95 (t, $J = 3.6$ Hz, 2H), 4.06-4.13 (m, 2H), 4.16-4.24 (m, 3H), 4.27 (s, 2H), 4.29 (d, $J = 1.4$ Hz, 2H), 6.89 (s, 1H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.57 (s, 2H), 7.85-7.91 (m, 3H); Unstable-trans 2.1 (Figure 2.4b): $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 218 K) $\delta$ 1.42 (d, $J = 6.4$ Hz, 3H), 1.93 (s, 3H), 2.50-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.1), 2.98 (dd, $J = 5.30$, 16.4 Hz, 1H), 3.42 (dd, $J = 8.2$, 16.3 Hz, 1H), 3.72-4.13 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.1), 4.20 (d, $J = 2.2$ Hz, 2H), 4.21-4.25 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.1), 4.28 (d, $J = 2.2$ Hz, 2H), 6.83 (s, 1H), 7.19-7.23 (m, 2H), 7.30 (t, $J$
Towards Dynamic Control of Wettability By Using Altitudinal Molecular Motors on Solid Surfaces

= 7.7 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.98 (s, 1H).

Irradiation experiment to generate unstable-cis 2.1:
Using the same procedure, no further changes were observed after 7 h of irradiation. The PSS ratio for stable-trans 2.1/unstable-cis 2.1 was determined to be 1/3.5 (Figure 2.4e). After warming the sample to rt, only the stable isomers were observed (Figure 2.4f). Stable-trans 2.1 (Figure 2.4d): 1H NMR (500 MHz, CD2Cl2, 218 K) δ 1.29 (d, J = 6.5 Hz, 3H), 2.09 (s, 3H), 2.52 (s, 1H), 2.57-2.60 (m, 2H), 3.28 (dd, J = 5.5, 14.7 Hz, 1H), 3.77-3.86 (m, 2H), 6.88 (s, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.3-7.34 (m, 2H), 7.65 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 8.09 (s, 1H); Unstable-cis 2.1 (Figure 2.4e): 1H NMR (500 MHz, CD2Cl2, 218 K) δ 1.45 (d, J = 6.4 Hz, 3H), 1.92 (s, 3H), 2.48-2.50 (m, 1H), 2.55-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-trans 2.1), 2.98 (dd, J = 5.3, 16.0 Hz, 1H), 3.41 (dd, J = 8.2, 16.3 Hz, 1H), 3.74-4.31 (absorptions in this region could not be resolved due to overlap with remaining stable-trans 2.1), 4.22 (d, J = 2.2 Hz, 2H), 6.83 (s, 1H), 7.30-7.35 (absorptions in this region could not be resolved due to overlap with remaining stable-trans 2.1), 7.39 (t, J = 7.7 Hz, 1H), 7.47 (s, 1H), 7.53 (dd, J = 0.7, 7.9 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 2H)

Irradiation experiment to generate unstable-trans 2.2:
Using the same procedure, no further changes were observed after 7 h of irradiation. The PSS ratio for stable-cis 2.2/unstable-trans 2.2 was determined to be 1/3.5 (Figure 2.5b). After warming the sample to rt, only the stable isomers were observed (Figure 2.5c). Stable-cis 2.2 (Figure 2.5a): 1H NMR (500 MHz, CD2Cl2, 218 K) δ 1.29 (d, J = 6.6 Hz, 3H), 2.06 (s, 3H), 2.52 (t, J = 2.3 Hz, 1H), 2.55-2.58 (m, 2H), 3.28 (dd, J = 5.3, 14.6 Hz, 1H) 3.79-3.85 (m, 2H), 3.9-4.0 (m, 4H), 4.10 (quin, J = 6.0 Hz, 1H), 4.14-4.25 (m, 2H), 4.26 (t, J = 2.4 Hz, 2H), 4.29 (d, J = 2.3 Hz, 2H), 6.88 (s, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.51 (s, 1H), 7.89-7.92 (m, 3H); Unstable-trans 2.2 (Figure 2.5b): 1H NMR (500 MHz, CD2Cl2, 218 K) δ 1.41 (d, J = 6.3 Hz, 3H), 1.95 (s, 3H), 2.50-2.51 (m, 1H), 2.55-2.59 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.2), 3.40 (dd, J = 8.4, 16.1 Hz, 1H), 3.72-4.29 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.2), 6.82 (s, 1H), 7.19-7.22 (m, 2H), 7.28-7.31 (m, 1H), 7.98 (s, 1H).
7.32-7.51 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.2), 7.82 (s, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.89-7.94 (absorptions in this region could not be resolved due to overlap with remaining stable-cis 2.2).

**Irradiation experiment to generate unstable-cis 2.2:**

Using the same procedure, no further changes were observed after 7 h of irradiation. The PSS ratio for stable-trans 2.2/unstable-cis 2.2 was determined to be 1/2 (Figure 2.5e). After warming the sample to rt, only the stable isomers were observed (Figure 2.5f). **Stable-trans 2.2** (Figure 2.5d): $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 218 K) $\delta$ 1.29 (d, $J = 6.6$ Hz, 3H), 2.09 (s, 3H), 2.52 (t, $J = 2.3$ Hz, 1H), 2.58 (d, $J = 14.7$ Hz, 1H), 2.59 (t, $J = 2.5$ Hz, 1H), 3.28 (dd, $J = 5.6$, 14.7 Hz, 1H), 3.77-3.86 (m, 3H), 3.94 (t, $J = 3.9$ Hz, 2H), 3.98-4.02 (m, 1H), 4.06 (t, $J = 6.5$ Hz, 1H), 4.17-4.32 (m, 2H), 4.24 (d, $J = 2.0$ Hz, 2H), 4.28 (d, $J = 2.3$ Hz, 2H), 6.87 (s, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.30-7.34 (m, 2H), 7.55 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 7.4$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 8.00 (s, 1H); **Unstable-cis 2.2** (Figure 2.5e): $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 218 K) $\delta$ 1.46 (d, $J = 6.2$ Hz, 3H), 1.89 (s, 3H), 2.49-2.51 (m, 1H), 2.55-2.60 (absorptions in this region could not be resolved due to overlap with remaining stable-trans 2.2), 3.00 (dd, $J = 5.7$, 16.4 Hz, 1H), 3.41 (dd, $J = 8.4$, 16.3 Hz, 1H), 3.74-4.32 (absorptions in this region could not be resolved due to overlap with remaining stable-trans 2.2), 4.22 (s, 2H), 6.83 (s, 1H), 7.19-7.39 (absorptions in this region could not be resolved due to overlap with remaining stable-trans 2.2), 7.37 (s, 2H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.87 (d, $J = 7.4$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 1H).

### 2.6.4 Preparation of the surface

**Preparation of azide terminated monolayer 2.13 SAM**

1.25 mL of the hydrolysis solution containing 11-azidoundecyltrimethoxy silane 2.13 (0.04 g), THF (6 ml), double-distilled H$_2$O (31 µl), and 37% HCl(aq.) (4 µl) was added to cyclohexane (25 mL) to give a slightly hazy solution. The piranha-cleaned quartz slides were immersed into this solution overnight. After the assembly the slides were sonicated in DMF, toluene and CH$_3$OH for 2 min each and dried under a stream of argon.
Preparation of the 2.1 MS and 2.2 MS
Compounds 2.1 and 2.2 were grafted to the 2.13 SAM by immersing this slide into a 1 mM solution of cis and trans isomers of 2.1 and 2.2 in DMF containing 1 mol% CuSO₄•5H₂O and 5 mol% sodium-ascorbate relative to the alkyne moieties. The azide functionalized slides were immersed for 12 h at rt. The modified quartz substrates (2.1 MS and 2.2 MS) were sonicated in DMF, water and CH₃OH for 2 min each and then dried under a stream of argon.

2.7 References


58


