Fluorinated light-driven molecular motors were synthesized and immobilized on gold in an altitudinal orientation via tripodal stators. In this design the functionalized molecular motors are not interfering and preserve their rotary function on gold. The wettability of the self-assembled monolayers can be switched by UV irradiation.

This chapter has been published:
Chapter 3

3.1 Introduction

One of the major challenges in nanotechnology is to demonstrate that molecular machines can be harnessed to perform useful work.\textsuperscript{[1]} Inspired by the machines of the macroscopic world, molecular tweezers, propellers, gears, brakes, elevators, valves, rotors, switches and nanocars have been developed.\textsuperscript{[2]} Additionally, it has been shown that molecular switches and motors can be used to perform various tasks in solution, such as reversible change in supramolecular organization,\textsuperscript{[3]} host-guest interactions,\textsuperscript{[4]} controlling the chiral space in which a catalytic reaction takes place,\textsuperscript{[5]} and synthesizing a peptide in a sequence-specific manner.\textsuperscript{[6]}

Confining molecules at an interface inhibits Brownian motion and allows for the modification of the surface properties of a material or even the possibility to perform work at the molecular level through externally induced reversible structural changes.\textsuperscript{[7]} In recent years, increasing attention has focused on surface-immobilized systems containing molecules that are capable of undergoing reversible structural changes upon the application of external stimuli.\textsuperscript{[8]} Various types of external stimuli, i.e. chemical,\textsuperscript{[9]} electric,\textsuperscript{[10]} or light\textsuperscript{[8a]}, can be applied to address molecules on surfaces. Among these stimuli the use of light, which allows spatiotemporal control,\textsuperscript{[11]} is of particular interest due to the potential fast response times of photochemical processes and because light provides a clean, noninvasive and tunable energy input.\textsuperscript{[12]}

Surfaces functionalized with photoresponsive azobenzene or spiropyran derivatives have been studied widely due to the propensity for these interfaces to undergo reversible light-induced wettability changes.\textsuperscript{[13]} Azobenzenes exhibit a change in conformation and dipole moment upon $E \rightarrow Z$ photoisomerization, resulting in changes to their polarity and accordingly the wettability of the surface.\textsuperscript{[14]} Spiropyrans can also be switched photochemically between a relatively hydrophobic spirocyclic and a hydrophilic merocyanine form, which induces a large change in molecular dipole moment.\textsuperscript{[15]} A number of approaches have been developed in order to enhance the wettability contrast between the two states of the azobenzene- and spiropyran-functionalized surfaces by using mixed layers,\textsuperscript{[16]} increasing surface roughness,\textsuperscript{[13a]} and using polymer-based surfaces.\textsuperscript{[17]} However, controlling the water contact angle (WCA) on flat and smooth surfaces functionalized with photoresponsive organic monolayers remains challenging. The change of the WCA of azobenzene monolayers is typically of the order of 2–14°,\textsuperscript{[18]} and 5–14°\textsuperscript{[19]} for spiropyran monolayers. Such modest changes encourage efforts to
design and study new responsive surfaces *via* the assembly of photochromic organic monolayers on flat substrates.

Light-driven molecular motors based on overcrowded alkenes\(^{[20]}\) are a unique class of organic molecules that are able to use light to power unidirectional rotation. When such molecules are attached to a surface, two types of orientation can be distinguished: azimuthal\(^{[21]}\) and altitudinal\(^{[22]}\) (Figure 3.1). Motors rotating in an altitudinal orientation relative to the surface have great potential for the construction of photoswitchable surfaces because the exposure of a functional group on the rotor can be switched in a cyclic fashion.\(^{[22d]}\) Despite the promise of altitudinal motors in powering surface-mounted nanomachinery, the speed of rotation has been shown to be affected by intermolecular interactions.\(^{[22b]}\) Although dilution (mixed monolayers) can minimize molecular interactions (but with the consequence of fewer molecular motors on the surface), the anticipated dynamic change in properties of these systems is reduced.

![Figure 3.1 Azimuthal (left) and altitudinal (right) rotary motors on surfaces.](image)

A key challenge in developing surface-bound devices based on molecular motors is to exploit the collective motion of the motor to interact with an external species in a dynamic manner. One way to demonstrate that the rotary motion of a surface-bound layer of oriented motors can collectively influence interactions with an overlayer material is to monitor the contact angle of a liquid on top of the motor monolayer. Changes in the contact angle of a liquid droplet at the surface of the
motor layer can be correlated to collective changes in the orientation of the rotor moieties with respect to the surface. Disruptive interactions between motors are expected to be minimized by designing motors with bulky stators that minimize the interaction between the rotor parts.

Light-driven, rotary, molecular-motor-based surfaces that undergo changes in wettability upon irradiation have not been reported to date. The wettability of a recently reported surface containing a monolayer of altitudinal motors was shown to depend on whether the motors were assembled in the cis or trans form.\(^{[22d]}\) However, once the motors were assembled, the wettability could not be modified, which was attributed to a lower photoconversion when motors are confined to a crowded monolayer compared to when in solution.

In this chapter we report a novel altitudinal light-driven molecular motor design comprising of a rotor with a hydrophobic perfluorobutyl group and a tripodal stator containing thiol groups for self-assembly on gold is described (Figure 3.1, right). The bulky stator increases the spacing between the rotors of the surface-bound motors sufficiently to facilitate unobstructed rotary motion. Water droplets placed on the motor-modified surfaces undergo changes in the contact angle upon irradiation of the surfaces with UV light. This is the first example showing that the wetting properties of surfaces functionalized with molecular motors based on overcrowded alkenes can be switched with light.

### 3.2 Design of tripodal molecular motors

The motor 3.8 (Scheme 3.1) was selected, as it exhibits a substantial barrier toward thermal isomerization,\(^{[23]}\) making this step slow at room temperature (rt) and thus facilitating characterization of the separate states during the rotary cycle in solution and on the surface. In addition, a hydrophobic perfluorobutyl group was incorporated onto the rotor part of the altitudinal motor in order to enhance the surface wettability changes upon switching.

A tripod\(^{[24]}\) was chosen as the surface anchoring group for the following reasons: (1) The rigid tripod is a promising stator to anchor the motor in a fixed and altitudinal orientation with respect to the surface; (2) as we reported previously, when the motor-embedded chromophores are assembled too close to the gold substrate (Figure 3.1, left, n=1), energy transfer from the excited state of the motor to the gold substrate may occur,\(^{[21a]}\) preventing the motor from rotating. Mounting the motor onto tripodal legs allows binding to gold in a rigid manner that is
expected to sufficiently isolate the motor from the surface, allowing efficient photoinduced isomerization (Figure 3.1, right); (3) it was previously shown that the attachment of overcrowded alkenes to surfaces via two-legs results in a high density of packing.\textsuperscript{[22b]} The increase of the half-life of the thermal isomerization step indicates intermolecular interactions between the surface-bound overcrowded alkenes, resulting in a decrease in the overall speed of the rotary cycle.\textsuperscript{[22b, 25]}

The bulky tripodal structure presented in this report is an ideal candidate to create free volume between the rotors, limiting interactions between the surface-bound motors and also enforcing altitudinal orientation. Calculations show that the area occupied by the tripod is expected to exceed the theoretical dimensions of the motor unit (Figure 3.2).

\textbf{Figure 3.2} B3LYP/6-31G(d,p) optimized structure for stable-\textit{cis} 3.1 (left) and stable-\textit{trans} 3.1 (right). H-atoms are all omitted.\textsuperscript{[†]}

\textsuperscript{†} Jos C. M. Kistemaker is acknowledged for the computational chemistry.
3.3 Synthesis of tripodal molecular motors

The approach toward the synthesis of motor 3.1, which bears a perfluorobutyl chain at the rotor and a tripod at the stator to allow surface attachment, is depicted in scheme 3.1.

Starting from 3.2, which was synthesized by a one pot Friedel-Crafts acylation / Nazarov cyclization, ketone 3.2 was subsequently brominated by treating it with four equiv of bromine in the presence of AlCl₃ in AcOH to form dibromosubstituted 3.3. The α-bromo substituent in 3.3 was removed by treatment with NaI and TMSCl in CH₃CN to form 3.4. The perfluorobutyl chain was introduced by treating 3.4 with nonafluoro-1-iodobutane and copper/bronze in DMSO, affording 3.5.

Ketone 3.5 was treated with Lawesson’s reagent in toluene to give the reactive thioketone 3.6. The key step in the synthesis of 3.8, which has a highly
sterically hindered double bond, is the Barton-Kellogg diazo-thioketone coupling. This coupling was performed by heating thioketone 3.6 and diazo compound 3.7 in toluene at reflux to afford overcrowded alkene 3.8 as a mixture of cis and trans isomers.

Motor 3.8 and tripod 3.9 were connected by a Sonogashira coupling in the presence of Pd(PPh₃)₄, providing 3.1 in 22% yield as a mixture of cis and trans isomers. Preparative thin layer chromatography provided pure stable-cis 3.1 and stable-trans 3.1. Their configuration was assigned by comparison of their ¹H NMR spectra with those of previously reported structurally related motors.[28]

3.4 Photochemical and thermal isomerization studies

Photochemical and thermal isomerization studies were carried out in solution using both low-temperature UV/vis absorption and ¹H NMR spectroscopy to demonstrate that stable-cis 3.1 and stable-trans 3.1 operate as molecular motors. [20]

The UV/vis absorption spectra of stable-cis 3.1 and stable-trans 3.1 in CH₂Cl₂ at 253 K both show absorption bands centered at 395 nm (Figure 3.3, solid lines).

![Figure 3.3 UV/vis absorption spectra (CH₂Cl₂, 253 K) of stable-cis 3.1 (a) and stable-trans 3.1 (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 3.1 to stable-trans 3.1 (a-2), and unstable-cis 3.1 to stable-cis 3.1 (b-2) via thermal isomerization at different temperatures.](image)
Irradiation of the same sample with UV light ($\lambda_{\text{max}} = 365$ nm) resulted in a red-shift of the band at 395 nm to an absorption centered at 450 nm, indicating the photochemically induced formation of the unstable isomers (Figure 3.3, dotted lines; Scheme 3.2, steps 1 or 3). This red-shift is consistent with increased strain at the central double bond, and hence the generation of a higher energy isomer.\textsuperscript{[29]} During the irradiation of each compound, isosbestic points were maintained indicating that the photoisomerization was a selective process.

Samples were irradiated until no further changes were observed, indicating that the photostationary state (PSS) was reached (Figure 3.3, dotted lines). Allowing the solutions to warm to rt resulted in a blue-shift of the band at 450 to 395 nm, which is consistent with thermal isomerization to the corresponding stable isomers (Figure 3.3, dashed lines; Scheme 3.2, step 2 or 4).

The activation parameters of the thermal isomerization from unstable-\textit{trans} 3.1 to stable-\textit{trans} 3.1 (Scheme 3.2, step 2) were determined at five temperatures (268, 273, 283, 288 and 293 K) in CH\textsubscript{2}Cl\textsubscript{2}. The thermal isomerization was followed by monitoring the change in absorption at 450 nm. Using the Eyring equation (Figure 3.3a-2), it was determined that this isomerization has a Gibbs free energy of activation ($\Delta^\ddagger G^\circ$) of 87.3 kJ/mol (unstable-\textit{trans} 3.1 $\rightarrow$ stable-\textit{trans} 3.1). This value corresponds to a half-life at rt of 402 s. Using the same procedure, the activation parameters of the thermal isomerization from unstable-\textit{cis} 3.1 to

\begin{center}
\textbf{Scheme 3.2} Full 360° rotary cycle for molecular motor 3.1 (R= 3.9, Scheme 3.1).
\end{center}
stable-cis 3.1 (Scheme 3.2, step 4) were determined at four temperatures (268, 273, 283 and 293 K) in CH$_2$Cl$_2$. The thermal isomerization was followed by monitoring the change in absorbance at 450 nm. Using the Eyring equation (Figure 3.3b-2), it was determined that this isomerization has a Gibbs free energy of activation ($\Delta^\ddagger G^0$) of 86.6 kJ/mol (unstable-cis 3.1 $\rightarrow$ stable-cis 3.1). This value corresponds to a half-life at rt of 307 s. These half-lives are similar to those obtained for structurally related motors.$^{[28]}$

The PSS ratio for stable-cis 3.1/unstable-trans 3.1 and stable-trans 3.1/unstable-cis 3.1 were determined by low temperature $^1$H NMR spectroscopy (Figure 2.4). 2 mg of stable-cis 3.1 was dissolved in 1 mL CD$_2$Cl$_2$ in an NMR tube and the $^1$H NMR spectra were recorded before, during and after UV irradiation ($\lambda_{max} = 365$) at 233 K. No further changes were observed after 6 h of irradiation. By comparing the integrals of the absorption of stable-cis 3.1 and unstable-trans 3.1 in the aliphatic and aromatic regions (Figure 3.4a and b; proton Ha, Hb, He, Hf and Hg; a photostationary ratio 18/82 for stable-cis 3.1/unstable-trans 3.1 (Scheme 3.2, step 1) was determined. Using the same procedure, the PSS ratio for stable-trans 3.1/unstable-cis 3.1 was determined to be 41/59 (Figure 3.4d and e; proton Ha, Hb, He, Hf and Hg; Scheme 3.2, step 3). After the samples containing the PSS mixtures were warmed to rt and kept at this temperature for 30 min, the samples were measured again at 233 K, the $^1$H NMR spectra showed quantitative conversion of the unstable isomers to the corresponding stable isomers (Figure 3.4c, b $\rightarrow$ c and e $\rightarrow$ f; scheme 3.2, step 2 and 4).

By studying the photochemical and thermal behavior of 3.1 in solution using a combination of UV/vis absorption and $^1$H NMR spectroscopy, and by analogy with similar motor systems reported previously,$^{[28]}$ it is concluded that 3.1 functions as a light-driven rotary motor in solution. In summary, the introduction of the tripod and a perfluorobutyl group on the motor moiety does not have a significant influence on the photochemical and thermal behavior of the motor.
Figure 3.4 Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 233 K) of 3.1 (a) stable-cis 3.1 (b) unstable-trans 3.1 formed upon UV irradiation to PSS (c) stable-trans 3.1 obtained after thermal isomerization of unstable-trans 3.1 at rt; (d) stable-trans 3.1 (e) unstable-cis 3.1 formed upon UV irradiation to PSS (f) stable-cis 3.1 obtained after thermal isomerization of unstable-cis 3.1 at rt. Signal assignments are given (R = 3.9, scheme 3.1).
3.5 Surface attachment and characterization

Immobilization of motor 3.1 on surfaces was achieved by immersion of a gold substrate in a solution of stable-cis 3.1 or stable-trans 3.1 with hydrazine as a deprotecting reagent. (Scheme 3.3, for further details on surface preparations, see experimental section) The mean monolayer thickness values of 16.9 ± 0.3 Å for stable-cis 3.1 SAM and 18.4 ± 0.1 Å for stable-trans 3.1 SAM were determined by XPS\(^{[30]}\) (see experimental section) and are in good agreement with similar overcrowded alkene systems assembled on a variety of surfaces previously reported by our group.\(^{[22a,25,31]}\) The surface coverage on gold (2.2×10\(^{-11}\) mol cm\(^{-2}\) for stable-cis 3.1 SAM and 2.4×10\(^{-11}\) mol cm\(^{-2}\) for stable-trans 3.1 SAM, as determined by UV/vis absorption spectroscopy, Figure 3.3 and 3.5) are consistent with monolayer formation.

![Scheme 3.3 Immobilization of molecular motor 3.1 onto a gold film.](image)

The UV/vis absorption spectra of stable-cis and stable-trans 3.1 SAMs showed the characteristic absorption of the motors after rinsing the substrates copiously with THF and CH\(_3\)OH, indicating that the attachment of motor 3.1 on the gold substrate was successful. (Figure 3.5, solid line). The major absorption bands (centered at 395 nm for stable 3.1 SAMs) are similar to those observed for 3.1 in CH\(_2\)Cl\(_2\) solution (Figure 3.3).
Irradiation of stable 3.1 SAMs with UV light ($\lambda_{\text{max}} = 365$ nm) resulted in a red-shift in the UV/vis absorption to 450 nm (Figure 3.5, lower panel) similar to that observed in CH$_2$Cl$_2$ solution (Figure 3.3), indicating the formation of the unstable form of the surface-bound motors (Scheme 3.2, steps 1 and 3). After keeping the surfaces in the dark at rt for 12 h, the original UV/vis absorption spectra recovered, which is consistent with the thermal isomerization of the motors (Figure 3.5, dashed line; Scheme 3.2, step 2 or 4).

In order to compare the surface-bound system with the solution analogue, we followed the thermal isomerization by monitoring the change in the UV/vis absorption spectra at 450 nm as a function of time. (Figure 3.6) The thermal decay of the signals were fitted with monoexponential decay, and the half-life for unstable-trans 3.1 SAM $\rightarrow$ stable-trans 3.1 SAM ($t_{1/2} = 530$ s at rt) and unstable-cis 3.1 SAM $\rightarrow$ stable-cis 3.1 SAM ($t_{1/2} = 351$ s at rt) were extracted. These values are similar to those observed in CH$_2$Cl$_2$ solution (Scheme 3.2, steps 2 and 4) showing that the thermal isomerization steps were not inhibited using the tripod as a surface attachment group and spacer between the motor and gold film.

The bulky structure of the tripod increases the distance between motor chromophores in the surface-bound monolayer, minimizing inter-rotor interactions.
Control of Surface Wettability Using Tripodal Light-Driven Molecular Motors

Figure 3.6 Thermal decay of UV/vis signals at 450 nm at rt during thermal isomerization of the motors as a function of time. (The black line is shown with an offset of +0.01)

The overview X-ray photoelectron (XPS) scans of the monolayers stable-cis 3.1 SAM and stable-trans 3.1 SAM before and after UV irradiation for 2 h are also shown in Figure 3.7. The spectra obtained after UV irradiation qualitatively resemble those collected on the pristine 3.1 SAMs, indicating the stability of the motor and tripod moieties on the gold surface under exposure to UV light for a considerable amount of time.

Figure 3.7 Overview XPS spectra of stable-cis 3.1 SAM (left) and stable-trans 3.1 SAM (right) before (red line) and after (black line) UV irradiation for 2 h, showing core level contributions of F 1s, O 1s, C 1s, S 2p and Au substrate 4p, 4d, 4f and 5p peaks. Au 4f doublet was truncated to facilitate observation of weaker lines.\(^\text{[6]}\)

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\(^\text{[6]}\) Dr. Oleksii Ivashenko is acknowledged for the characterization of 3.1 SAMs by XPS.
Water contact angle (WCA) measurements were performed on motor 3.1 SAM on flat gold (150 nm Au/mica) in order to determine the wettability of the monolayers. In the case of stable-cis 3.1 SAM, where the hydrophobic perfluorobutyl group is likely to be hidden from the interface, a contact angle of 60 ± 1° was measured; however, stable-trans 3.1 SAM, where the perfluorobutyl groups are exposed to the interface, shows a contact angle of 82 ± 1° (Figure 3.8), which is attributed to the hydrophobic nature of the perfluorobutyl chain.

![Figure 3.8 Water droplet on stable-cis 3.1 SAM (left) and stable-trans 3.1 SAM (right).](image)

In the present system using an altitudinal molecular motor, control of surface wettability was achieved by irradiating both 3.1 SAMs with UV light (\(\lambda_{\text{max}} = 365\) nm), which resulted in WCA changes of the stable-cis 3.1 SAM from 60 ± 1° to 76 ± 1° and for the stable-trans 3.1 SAM, 82 ± 1° to 68 ± 1°. (Table 3.1). The changes in WCA after UV irradiation are a manifestation of the photoinduced switching of the motors on gold and are consistent with UV/vis spectroscopic data (Figure 3.6).

Table 3.1 Water contact angle for stable-cis 3.1 SAM and stable-trans 3.1 SAM before and after UV irradiation on flat surface.

<table>
<thead>
<tr>
<th>Contact Angle (°)</th>
<th>before irradiation</th>
<th>after irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable-cis 3.1 SAM</td>
<td>60 ± 1</td>
<td>76 ± 1</td>
</tr>
<tr>
<td>Stable-trans 3.1 SAM</td>
<td>82 ± 1</td>
<td>68 ± 1</td>
</tr>
</tbody>
</table>

The ratios between stable-cis 3.1 and unstable-trans 3.1 or stable-trans 3.1 and unstable-cis 3.1 are 18:82 or 41:59 in solution, respectively, at the photostationary state (PSS\(_{365\text{ nm}}\), Scheme 3.2, steps 1 or 3). The separation between the molecular motors and the surface as well as each other achieved with the present immobilization approach means that it would be reasonable to expect that the PSS achieved in solution is retained in the SAMs also. Indeed, on the first cycle the changes observed are consistent with the PSS observed in solution. Hence, upon irradiation of the molecular motors anchored on the surface, the
changes in wettability are not expected to show full reversibility over several cycles but instead reach an intermediate situation between purely cis- and trans-states, as is observed experimentally (Figure 3.9). These data demonstrate that the design employed in anchoring the molecular motor to the surface allows light to be used to change molecular state and thereby achieve the highly challenging task of changing wettability with an external stimulus.

![Figure 3.9 Water contact angle of stable-cis 3.1 SAM and stable-trans 3.1 SAM as a function of UV irradiation cycle.](image)

Modifying the wettability of a substrate with a monolayer of rotary motors upon irradiation is unprecedented. Previously, surfaces functionalized with cis or trans isomers of altitudinal motors with the same perfluorobutyl chain on the rotor as reported here showed only a difference of 12° in WCA between the cis and trans surfaces, and the surface wettability could not be modified by UV irradiation.\(^{22d}\) Presumably, without the bulky tripod spacer the motor chromophores are too crowded to allow for a sufficient yield of photoisomerization to detect an appreciable change in macroscopic properties.\(^{22d}\)

Incorporating three phenyl-acetylene-based “legs” into the structure of the motor increases the space between the rotors, allowing for facile rotary motion and hence modification of the surface properties.
3.6 Conclusions

Motors bearing a hydrophobic perfluorobutyl group on the rotor and rigid phenyl-acetylene-based tripod on the stator were successfully synthesized and attached to a gold surface.

The spacing between the motor and the gold surface is sufficient to effectively compete with quenching of the excited state by the gold surface and to allow for photoisomerization of the central alkene. Confinement of altitudinal motors at surfaces via flexible long chains was reported to reduce the rate of the thermal isomerization process,\cite{22b} however, the system described herein has overcome this issue. In the present system the thermal isomerization is not inhibited, showing that the tripod is an ideal surface anchoring group to prevent the motors from interacting with each other and from interacting directly with the underlying gold substrate.

Additionally, although previously reported nonsymmetric altitudinal motors bearing fluoro groups were unable to change the water contact angle by irradiation post-assembly, the current system can change the contact angle of a water drop by up to 16° upon irradiation of the motor-water interface. This is the first example of controlling the surface wettability of a monolayer of motors by irradiation. The tripod structure minimizes obstruction of the rotary cycle and enhances the ability to modulate collective interactions at the motor–water interface. The current design features will be key to fabricating future nanoscale systems that can be used to exploit the rotary cycle to perform work at the molecular level, to control interactions with surface adsorbates and to apply single molecule techniques to measure the rotation of a single motor on a surface.
3.7 Experimental Section

3.7.1 General remarks
For general remarks on the synthesis and characterization of compounds and intermediates, see Chapter 2. All UV/Vis absorption spectra in solution were recorded by Hewlet-Packard HP 8543 diode array. To generate the unstable form of the motor, samples were irradiated with UV light (Spectroline model ENB-280C/FE lamp, $\lambda_{\text{max}} = 365$ nm) at a distance of 3 cm from the centre of the lamp.

3.7.2 Synthesis of compounds and intermediates

**Compound 3.3**
To a solution of 3.2 (7.2 g, 36.7 mmol) in acetic acid (100 mL) AlCl$_3$ was added (0.5 g, 3.6 mmol), the solution was stirred vigorously at 40 °C for 1 h until most of the AlCl$_3$ was dissolved. Then Br$_2$ (23.5 g, 146.9 mmol) was added dropwise to the mixture and stirred at 40 °C for 1 d. The mixture was cooled to rt, diluted with EtOAc (200 mL) washed with aqueous Na$_2$S$_2$O$_3$ (sat.) (2×50 mL), water (100 mL), brine (50 mL) and then dried (Na$_2$SO$_4$) before being concentrated in vacuo. Recrystallization from dichloromethane and pentane afforded 3.3 as a light orange solid. (5.2 g, 14.7 mmol, 40%). M.p. 70 – 72 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.02 (s, 1H), 3.62 (d, $J = 18.6$ Hz, 1H), 3.92 (d, $J = 18.6$ Hz, 1H), 7.52–7.59 (m, 2H), 7.88 (d, $J = 7.5$ Hz, 1H), 8.58 (d, $J = 8.7$ Hz, 1H), 9.14 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 27.4, 46.6, 59.9, 123.5, 124.0, 124.9, 127.2, 130.1, 131.5, 131.6, 131.9, 136.4, 153.0, 200.6; HRMS (EI-ion trap) $m/z$: [M]+ Calcd for C$_{14}$H$_{10}$Br$_2$O 351.9098, found 351.9110.

**Compound 3.4**
A solution of 3.3 (4.08 g, 11.5 mmol) in acetonitrile (130 mL) was added to a stirred solution of sodium iodide (5.1 g, 34.3 mmol) in acetonitrile (30 mL). The mixture was stirred at rt for 30 min, chlorotrimethylsilane (3.1 g, 28.9 mmol) was added and the mixture was further stirred for 2 h at rt. The mixture was diluted with EtOAc (200 mL) washed with aqueous Na$_2$S$_2$O$_3$ (sat.) (2×50 mL), water (100 mL), brine (50 mL), dried (Na$_2$SO$_4$) and then concentrated in vacuo affording 3.4 as a white solid (3.2 g, 11.5 mmol, 96%). M.p. 72 – 74 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.38 (d, $J = 7.3$ Hz, 3H), 2.73–2.92 (m, 2H), 3.50 (dd, $J = 18.3, 8.2$ Hz, 1H), 7.46–7.53 (m, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.84 (dd, $J = 7.5, 0.8$ Hz, 1H),
8.49 (d, \( J = 8.7 \text{ Hz}, \ 1\text{H} \)), 9.19 (d, \( J = 8.4 \text{ Hz}, \ 1\text{H} \)); \(^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3 \)) \( \delta \) 16.7, 35.1, 42.7, 123.0, 123.7, 125.3, 129.3, 130.3, 130.7, 131.0, 131.2, 134.6, 157.1, 209.5; HRMS (EI-ion trap) \( m/\text{z} \): [M]\(^+\) Calcd for C\(_{14}\)H\(_{11}\)BrO 273.9993, found 273.9982.

**Compound 3.5**

A suspension of activated copper-bronze (2.8 g, 44.1 mmol) in dry DMSO (80 mL) was heated to 130 °C for 15 min. Nonatafluoro-1-iodobutane (7.6 g, 21.9 mmol) was added dropwise and the mixture was stirred at 130 °C for 45 min. Ketone 3.4 (1.2 g, 4.7 mmol) in DMSO (80 mL) was added dropwise and the mixture was stirred for an additional 3 h at the same temperature. The mixture was diluted with diethyl ether (100 mL) and filtered over celite to remove copper-bronze. The organic phase was washed with water (2×100 mL), brine, dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. The crude product was purified by column chromatography (SiO\(_2\), 7:3 pentane:CH\(_2\)Cl\(_2\)) to give 3.5 (670 mg, 1.6 mmol, 37%) as a dark oil. \(^1\text{H} \text{ NMR (500 MHz, CDCl}_3 \)) \( \delta \) 1.39 (d, \( J = 7.3 \text{ Hz}, \ 3\text{H} \)), 2.89-2.79 (m, 2H), 3.50 (dd, \( J = 18.2, 8.1 \text{ Hz}, \ 1\text{H} \)), 7.64 (d, \( J = 9.0 \text{ Hz}, \ 1\text{H} \)), 7.75 (t, \( J = 7.9 \text{ Hz}, \ 1\text{H} \)), 7.88 (d, \( J = 7.4 \text{ Hz}, \ 1\text{H} \)), 8.43 (d, \( J = 8.9 \text{ Hz}, \ 1\text{H} \)), 9.54 (d, \( J = 8.4 \text{ Hz}, \ 1\text{H} \)); \(^{13}\text{C} \text{ NMR (75 MHz, CDCl}_3 \)) \( \delta \) 209.6, 156.5, 131.9, 131.9, 131.8, 131.8, 130.7, 130.4, 129.4, 128.9, 128.4, 128.2, 128.1, 127.3, 125.8, 42.5, 34.9, 16.5; HRMS (ESI-ion trap) \( m/\text{z} \): [M]\(^+\) Calcd for C\(_{18}\)H\(_{11}\)F\(_9\)O 415.0739, found 415.0733.

**Compound 3.8**

To a solution of 3.5 (287 mg, 0.7 mmol) in toluene (10 mL) was added Lawesson’s reagent (476.3 mg, 1.2 mmol). The mixture was heated at 90 °C for 3 h. The toluene was distilled off in vacuo and the residue was purified by column chromatography (pentane:CH\(_2\)Cl\(_2\), 1:1). The first wine-red band was collected (92 mg, 0.2 mmol), concentrated and added immediately to a solution of 3.7 (123.6 mg, 0.4 mmol) in toluene (30 mL). The mixture was heated at 90 °C for 12 h then cooled down to rt and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO\(_2\), 1:4 pentane:CH\(_2\)Cl\(_2\)) affording 3.8 (52 mg, 0.076 mmol, 37%, mixture of cis and trans isomers) as yellow sticky oil. The trans and cis isomers can be separated by column chromatography (SiO\(_2\), 10:1 pentane:ether). **Stable-trans 3.8**: \(^1\text{H} \text{ NMR (400 MHz, CD}_2\text{Cl}_2 \)) \( \delta \) 1.40 (d, \( J = 6.7 \text{ Hz}, \ 3\text{H} \)), 2.84 (d, \( J = 15.4 \text{ Hz}, \ 1\text{H} \)), 3.62 (dd, \( J = 15.3, 5.4 \text{ Hz}, \ 1\text{H} \)), 4.36-4.27 (m, 1H), 6.58 (d, \( J = 7.9 \text{ Hz}, \ 1\text{H} \)), 6.82 (t, \( J = 7.5 \text{ Hz}, \ 1\text{H} \)), 7.24 (t, \( J = 7.4 \text{ Hz}, \ 1\text{H} \)),
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7.40 (t, J = 7.9 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.2 Hz, 3H), 7.85 (d, J = 7.2 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.42-8.28 (m, 2H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 19.4, 42.4, 46.1, 92.6, 119.8, 121.9, 125.6, 125.8, 126.4, 127.1, 127.9, 128.0, 128.1, 128.2, 129.8, 130.6, 131.1, 132.8, 133.8, 135.29, 136.1, 136.4, 137.1, 137.5, 139.4, 142.2, 148.7, 152.6; $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -81.33, -103.90, -121.09, -125.72.

Stable-cis 3.8: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 1.36 (d, J = 6.2 Hz, 3H), 2.80 (d, J = 15.5 Hz, 1H), 3.56 (dd, J = 15.5, 5.7 Hz, 1H), 4.39-4.25 (m, 1H), 6.78 (s, 1H), 7.53-7.34 (m, 5H), 7.71 (d, J = 8.8 Hz, 1H), 7.81-7.77 (m, 1H), 7.85 (d, J = 7.4 Hz, 1H), 7.96 (d, J = 8.1 Hz, 2H), 8.31 (d, J = 8.9 Hz, 1H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 19.4, 42.3, 45.8, 91.3, 120.4, 121.2, 124.8, 125.5, 125.6, 125.7, 126.3, 127.9, 128.0, 128.1, 128.2, 128.3, 129.7, 130.3, 131.0, 132.7, 133.8, 135.3, 136.1, 137.3, 139.2, 139.6, 139.7, 148.6, 152.7; $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -81.23, -104.10, -121.11, -125.65.

Stable-trans 3.1: $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 1.49 (d, J = 6.7 Hz, 2H), 2.40 (s, 9H), 2.89 (d, J = 15.2 Hz, 1H), 3.68 (dd, J = 15.2, 5.4 Hz, 1H), 4.15 (s, 6H), 4.49-4.43 (m, 1H), 6.64 (d, J = 7.9 Hz, 1H), 6.85 (t, J = 7.7 Hz, 1H), δ 7.89 (dd, J = 13.8, 7.6 Hz, 2H), 7.81 (dd, J = 15.6, 8.3 Hz, 15H), 7.72-7.65 (m, 5H), 7.65-7.57 (m, 6H), 7.55-7.50 (m, 4H), 7.50-7.41 (m, 6H), 7.38-7.27 (m, 10H), 8.14 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 8.37 (d, J = 8.6 Hz, 1H); $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -81.23, -103.83, -120.92, -125.76; UV/vis (CH$_2$Cl$_2$, 253 K): $\lambda_{max}$ (ε) = 395 nm (19166 M$^{-1}$cm$^{-1}$).

Compound 3.1

A mixture of stable-cis 3.8 and stable-trans 3.8 (53.7 mg, 58.1 mmol), 3.9 (40 mg, 58.1 mmol), Ag$_2$O (8.1 mg, 34.8 mmol), Cs$_2$CO$_3$ (11.4 mg, 34.8 mmol) and Pd(PPh$_3$)$_4$ (3.4 mg, 2.9 mmol) was stirred in dry THF (6 mL) at 90 °C for 12 h. After the mixture was cooled to rt, it was diluted with diethyl ether (6 mL) and filtered over a plug of celite. After removal of all volatiles in vacuo, the product was purified by column chromatography (SiO$_2$, 1:5 pentane:CH$_2$Cl$_2$), yielding a yellow oil (19 mg, 12.8 mmol, 22%, mixture of cis and trans isomers). The cis and trans isomers were separated by preparative thin layer chromatography (Silica gel, 1:1 hexane:tert-butyl methyl ether). Stable-cis 3.1: $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 1.46 (d, J = 6.7 Hz, 3H), 2.40 (s, 10H), 2.89 (d, J = 15.4 Hz, 1H), 3.67 (dd, J = 15.6, 5.7 Hz, 1H), 4.16 (s, 8H), 4.47-4.41 (m, 1H), 6.77 (s, 1H), 7.39-7.28 (m, 10H), 7.56-7.41 (m, 14H), 7.69-7.56 (m, 17H), 7.81 (d, J = 8.2 Hz, 2H),
7.91 (d, $J = 7.1$ Hz, 2H), 8.07 (d, $J = 7.3$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 8.39 (d, $J = 8.8$ Hz, 1H); $^1$H NMR (376 MHz, CD$_2$Cl$_2$) δ -81.15, -103.83, -120.92, -125.76; UV/vis (CH$_2$Cl$_2$, 253 K): $\lambda_{\text{max}}$ (ε) = 395 nm (15724 M$^{-1}$cm$^{-1}$). Stable-3.1: $^{13}$C NMR (101 MHz, CDCl$_3$) δ 19.1, 19.3, 22.7, 29.7, 30.3, 33.1, 41.8, 41.9, 45.2, 45.5, 88.8, 89.1, 89.4, 90.3, 90.4, 91.3, 92.1, 119.1, 119.5, 119.7, 120.1, 120.3, 120.4, 121.2, 121.4, 123.4, 123.5, 124.2, 124.7, 124.8, 125.0, 125.1, 125.4, 125.6, 127.4, 127.6, 128.4, 128.7, 128.9, 129.0, 129.2, 130.3, 130.5, 130.6, 130.7, 130.8, 131.0, 131.1, 131.7, 132.0, 132.2, 133.0, 133.4, 133.6, 133.7, 135.1, 135.9, 136.1, 136.2, 136.6, 136.9, 137.1, 137.3, 138.0, 138.0, 139.1, 139.5, 139.7, 139.9, 140.2, 147.6, 147.7, 151.4, 151.4, 194.9; HRMS (APCI-ion trap) m/z: [M + Na]$^+$ Calcd for C$_{90}$H$_{61}$F$_9$O$_3$S$_3$SiNa 1507.3300, found 1508.3337.

3.7.3 Preparation of the 3.1 SAMs

Method A: Quartz microscope slides (Ted Pella, Inc.) were cut into 1×2.5 cm$^2$ pieces, cleaned by immersing in a piranha solution at 90 ºC for 1 h and rinsed copiously first with doubly distilled water (3 times), then with CH$_3$OH and dried under a stream of N$_2$ before surface modification. (Caution! Piranha solution is highly corrosive and reactive toward organics) Before gold deposition the piranha-cleaned quartz slides were silanized rather than using chromium as the adhesive coating in order to increase the optical transparency of the substrate. For this, the slides were immersed in 1 mM solution of 3-aminopropyl(diethoxy)methylsilane in freshly distilled toluene for 12 h, then copiously rinsed with toluene and methanol, sonicated first in toluene, then in methanol and dried under a stream of N$_2$.

Au films were prepared by vapour deposition of a 5 nm thick layer of gold (purity 99.99%, Schöne Edelmetall B.V.) on the 3-aminopropyl(diethoxy)methylsilyl functionalized slides in a custom-built high-vacuum evaporator (base pressure 10$^{-7}$ mbar). The UV/Vis absorption spectrum of this semi-transparent gold film is shown (Figure 3.11). 20 mL solution of THF containing stable-cis 3.1 or stable-trans 3.1 (5 mM) was purged with argon for 1 h and then hydrazine monohydrate (20 µL) was added. The gold film was immersed in this solution at rt for 16 h. The slides were removed, washed with THF, CH$_3$OH and dried under a stream of argon. The SAMs prepared this way were used for UV/Vis absorption spectroscopic studies.
**Method B:** Au films on mica were prepared by vapour deposition of 150 nm thick films of Au in a custom-built high-vacuum evaporator (base pressure $10^{-7}$ mbar). Prior to vapour deposition, mica sheets were freshly cleaved and annealed at 375 °C for 16 h in order to remove impurities. 20 mL solution of THF containing stable-cis 3.1 or stable-trans 3.1 (5 mM) was purged with argon for 1 h and then hydrazine monohydrate (20 µL) was added. The clean substrate was immersed immediately after gold deposition in this solution at rt for 16 h. Subsequently, the slides were removed, washed with THF, CH$_3$OH, and dried under a stream of argon. The SAMs prepared this way were used for XPS studies and contact angle measurements.

![UV/Vis absorption spectrum](image)

**Figure 3.10** UV/Vis absorption spectrum of the semi-transparent gold film on glass which displays a plasmon band around 600 nm in accordance with a gold film of this thickness prepared on silanated quartz.

### 3.7.4 Characterization of the 3.1 SAMs

**UV/Vis absorption spectroscopy of the 3.1 SAMs on a gold surface**

UV/Vis absorption spectra were recorded using a Jasco V-630 spectrophotometer under N$_2$ atmosphere. (Scan rate 100 nm/min; Band Width 1.0 nm, N$_2$ atmosphere was used for baseline correction). The samples were irradiated with UV light (spectroline model ENB-280C/FE lamp, $\lambda_{max} = 365$ nm) at a distance of 3 cm.
Determining the thickness of the 3.1 SAMs from XPS results

The thickness of the self-assembled monolayers were calculated from the attenuation of the Au 4f XPS signal of the substrate. A clean substrate shows integrated intensity $I_{Au0}$. Due to grafting of the tripod molecules which form a film of thickness $d$, the integrated intensity $I_{Au}$ of substrate decreases according to Equation 3.1, where $\theta$ is the angle of the detector with respect to the normal to the surface (37º) and $\lambda$ is the attenuation length of photoelectrons in hydrocarbon SAMs (42 Å).

$$I_{Au} = I_{Au0}\exp(-d/\lambda \sin \theta) \quad \text{(Eq. 3.1)}$$

We found film thicknesses of 16.9 ± 0.3 Å for the stable-cis 3.1 SAM and of 18.4 ± 0.1 Å for stable-trans 3.1 SAM, respectively. These thicknesses agree with single layers of tripod molecules present on the surface.

Contact angles measurements

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 µL water droplets on stable-cis 3.1 SAM or stable-trans 3.1 SAM using the sessile drop method. The contact angle was measured at two different locations on each surface and the results were averaged. For the irradiation experiment, a molecular motor 3.1 functionalized slides were transferred into a vial capped with a septum purged with argon and irradiated with UV light (Spectroline model ENB-280C/FE lamp, $\lambda_{max} = 365$ nm) at a distance of 3 cm for 20 min. After measuring the WCA of the irradiated surface, the slide was incubated in the dark for 12 h. The slide was then irradiated again prior to taking the CA, which was measured in the same manner as described above. The procedure was repeated once more.
3.8 References


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