Chapter 1
Light-Driven Molecular Motors on Surfaces

Confining light-driven molecular motors on surfaces could inhibit the Brownian motion and hence, the relative rotation of one part of the molecule with respect to the other can be converted into absolute rotation.
1.1 Introduction

The design and construction of molecular-level devices e.g., molecular switches and machines for the control over macroscopic phenomena is of great importance to future nanotechnologies\textsuperscript{[1,2,3,4,5,6,7]}. Nature provide chemists with fascinating examples of nanoscale rotary motors, F\textsubscript{1}-ATP synthase\textsuperscript{[8]}, of which solvated form is able to hydrolyze adenosine tri-phosphate (ATP), the cell’s energy currency, and convert the energy into rotary motion of its central stalk\textsuperscript{[9,10]}. Inspired by the dynamic systems like naturally occurring ATP synthase and the machines of the macroscopic world, scientists have developed molecular tweezers\textsuperscript{[11]}, propellers\textsuperscript{[12]}, brakes\textsuperscript{[13]}, elevators\textsuperscript{[14]}, nanocars\textsuperscript{[15,16]} and muscles\textsuperscript{[2]} over the past decades\textsuperscript{[7,17,18]}. Moreover, it has been demonstrated that molecular switches can be used to perform specific functions, such as reversible change in supramolecular organization\textsuperscript{[19]}, synthesizing a peptide in a sequence-specific manner\textsuperscript{[20]}, rotating microscale objects\textsuperscript{[21]} and control of singlet oxygen generation for photodynamic therapy\textsuperscript{[22]}.

While in the solution phase, any directed motion generated by the molecular machines is overwhelmed and dissipated by the uncontrolled Brownian motion, which makes it challenging to harness the collective motion of molecular machines to perform work. Immobilizing molecules on the interface inhibits the Brownian motion and allows not only for tuning the surface with tailored properties e.g., wettability\textsuperscript{[1,2,4,24]}, optical property\textsuperscript{[1,2,6]}, conductance\textsuperscript{[1,7]}, chirality\textsuperscript{[2,3]}, and catalytic activity\textsuperscript{[1,3]} but also for performing work at the molecular level through externally induced reversible structural changes\textsuperscript{[33,34,35]}.

In recent years, increasing attention has therefore been focused on surface-immobilized systems containing molecules that are capable of undergoing reversible structural changes in response to external stimuli\textsuperscript{[36,37]}. Spiropyans, azobenzenes, dithienylethenes, and molecular motors based on overcrowded alkenes have proven to be particularly versatile stimuli-responsive molecules in surface-immobilized systems\textsuperscript{[3,4,7]}. Various types of external stimuli e.g., chemical\textsuperscript{[38,39]}, electric\textsuperscript{[40]} or light\textsuperscript{[36]} can be applied to change the structure of these molecules on the surfaces. Among these stimuli the use of light, which allows spatial temporal control\textsuperscript{[26]} 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{[41]}. In this chapter, we focus on various approaches for the control of surface wettability using surface-immobilized
systems based on photochromic molecular switches. Furthermore a detailed review and analysis of the recent progress in photoresponsive surface based on molecular motors, and their potential applications in the control of surface wettability is presented.

1.2 Photochromic molecular switches

1.2.1 Spiropyans

The ring-closed form of spiropyran is consisting of an indoline and a chromene moiety bound together via a spiro junction making the two moieties oriented perpendicularly to with each other (Scheme 1). Spiropyran could undergo photoisomerization from a ring-closed form (SP) to a zwitterionic merocyanine isomer (MC) upon irradiation with UV light, which is accompanied with a large change in dipole moment (~15 Debye).\[^7,42,43\]

![Scheme 1](image)

Scheme 1 Reversible isomerization between ring-closed form and merocyanine form of spiropyran.\[^{[*]}\]

1.2.2 Azobenzenes

Azobenzenes are among the most studied photochromic units and have received substantial attention due to their simple molecular structure, relatively facile synthesis, and fatigue resistant trans→cis photoisomerization.\[^7,44,45\] When the thermodynamically stable trans isomer of azobenzene is exposed to UV light, it isomerize to the cis isomer (Scheme 2); the two isomers have noticeable difference in molecular geometry, electronic properties, and dipole moment, making azobenzene an attractive candidate for construction of photoswitchable systems

\[^{[*]}\] For consistency, the name “spiropyran” in this chapter applies to both isomers, and the ring-closed form is abbreviated as “SP”, ring-open form as “MC”.

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\[^7\] N
\[^8\] R
\[^9\] O
\[^{NO2}\]

Spiropyran (SP)

\[^{UV, \Delta}\]

Spiropyran (MC)

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and materials. The cis isomer is metastable, hence it undergoes thermal cis→trans isomerization at room temperature once the UV light source is removed and this may be the drawback in the construction of photoresponsive surfaces based on azobenzenes.

Scheme 2 Reversible photoisomerization of azobenzene moieties upon UV-vis irradiation.

1.2.3 Dithienylethenes

Dithienylethenes undergo photocyclization from ring-open to closed form by irradiation with UV light (300 < λ < 400 nm); while the reverse process occurs with visible light (500 < λ < 700 nm).\(^7\) In the ring-closed form of dithienylethene, the π-conjugation extends through the entire molecule; while in the ring-open form, it is restricted to each half of the molecule (Scheme 3). Compared to other photochromic compounds, dithienylethenes display excellent thermal stability for both isomers as well as superb resistance to photodegradation.\(^{46,47}\)

Scheme 3 Photoswitching of dithienylethenes.

1.2.4 Alkenes

Olefins can undergo trans→cis photoisomerization through a geometrical isomerization of the C=C double bond.\(^{48}\) The best known switch among these systems are stilbenes, which can be switched reversibly between trans and cis isomers upon irradiation with light (Scheme 4).\(^{7,49}\) However, the application of stilbenes for the construction of a photoresponsive surface is limited due to side
reactions. Photochemical reaction of cis-stilbene results in an oxidative cyclization to provide phenanthrene, a side product that could not be reverted to its original form. This side reaction could be prevented by ortho-substitution of the benzene rings which forms the basis for the construction of molecular motors based on overcrowded alkenes (see section 1.4 for discussions on molecular motors).

![Scheme 4](image)

**Scheme 4** Photoisomerization of stilbenes and the side reaction: oxidative photocyclization.

### 1.3 Controlling of surface wettability with molecular switches

One of the simplest way to demonstrate that the photoinduced switching of a surface-bound layer of molecular switches can collectively influence interactions with an overlayer material is to monitor the contact angle of a liquid on top of the monolayer of molecular switches. Changes in the contact angle (CA) of a liquid droplet at the surface of the monolayer can be correlated to collective changes in the orientation or morphology of the switches with respect to the surface. Numerous examples of surfaces functionalized with photo-responsive molecular switches and machines for reversible light-induced wettability changes have been reported and representative examples are discussed below.

#### 1.3.1 Spiropyran-functionalized surfaces

Spiropyrans can be converted from a relatively hydrophobic ring-closed form (SP) to a hydrophilic zwitterionic merocyanine isomer (MC) accompanied with a higher dipole moment (Scheme 1). This unique feature makes spiropyrans ideal candidates for controlling surface wettability by light. Rasario et al. demonstrated that the water contact angle (WCA) of a droplet on a surface functionalized with mixed monolayers of spiropyrans and alkylsilanes can be switched reversibly upon irradiation with UV and visible light (Figure 1). They further demonstrated that by coating a similar monolayer in the inner wall of a 500 µm diameter capillary, the water in the capillary tubes rose up for ~2.8 mm upon UV irradiation, while the
water did not rise using a control capillary tube.\textsuperscript{[52]}

![Figure 1](image)

**Figure 1** Water droplet on a spiropyran-functionalized surface after irradiation with visible light (left) and UV light (right). The magnitude of the WCA change was found to be 11°–14°. Reproduced from Ref. [42,52].

However, the control of WCA on flat and smooth surfaces functionalized with photoresponsive organic monolayers remains challenging. The change of the WCA of spiropyran monolayers on flat surfaces is typically in the order of 5–14°.\textsuperscript{[42,52]} Therefore, different strategies have been applied in an effort to amplify the contact angle variation. Locklin *et al.* reported a surface modified with covalently attached spiropyran-based polymer films which could be used to switch the WCA reversibly for up to 15° upon UV irradiation.\textsuperscript{[53]} By simply adding CoCl\textsubscript{2} to the water droplet lying on the same polymer film, the WCA variation could be enhanced from 15° to 35° upon UV irradiation (Figure 2). This amplification of WCA change is attributed to the photoisomerization from SP→MC•Co(II) instead of SP→MC; with the MC•Co(II) being a more hydrophilic complex. A drawback of this approach is the potential contamination of the surface with CoCl\textsubscript{2} salt.
Inspired by the naturally occurring superhydrophobic surfaces, e.g. lotus leaves, butterfly wings and water striders, an alternative approach to enhance the contact angle change is achieved by combining two features together: the chemical composition of the surface and the surface roughness. A rough surface could be prepared by modifying the surface either with Si-nanowires (20-50 nm diameter; Figure 3, left) or polymeric nanorods (Figure 3, right). It is generally assumed that for rough surfaces with water repellent properties, the liquid droplets rest on top of the rough features with air trapped in the nanopores (Cassie wetting), while for the enhanced wettability of a hydrophilic surface, the droplets penetrate and wet the rough features of the surfaces (Wenzel wetting).

Yang et al. found that by grafting polymers with spiropyran side chains on a silicon substrate, the WCA of this rough surface could be changed from 140° to 43° upon UV irradiation and be changed back after 20 min of irradiation with visible light (Figure 4). Chen et al. demonstrated a synergistic system based on cross-linked poly(N-Isopropyl Acrylamide) copolymer film containing covalently
attached spiropyrans (pNIPAAm-SP).[59] The surface was initially rich in pNIPAAm-MC•H⁺ in the hydrated form in dark environment, the photoisomerization of pNIPAAm-MC•H⁺→pNIPAAm-SP upon irradiation with visible light triggered the dehydration of the main chain of pNIPAAm, resulting the WCA to change from 49º to 73º. The authors further demonstrated that by incorporating microstructures[63] or nanostructures with nanorods[64] to the surface, the WCA variation could be enhanced from ~24º to ~79º and ~118º, respectively.

![Figure 4](image)

**Figure 4** Water droplet on silicon substrates functionalized with spiropyran polymers before (left) and after (right) UV irradiation. Reproduced from Ref. [62].

### 1.3.2 Azobenzene-functionalized surface

Azobenzene exhibits changes in conformation and dipole moment upon trans→cis photoisomerization, resulting in changes to the inherent polarity and accordingly the surface wettability while attached to the interface (Scheme 2). Generally the WCA of trans-azobenzene monolayers decrease after UV irradiation, since the photoinduced cis isomer usually has a higher dipole moment, which is attributed to the asymmetric bent structure and the electron withdrawing properties of the N=N moiety of the azobenzenes in the cis form.[44,65]

Tamaki *et al.* compared the WCA changes of self-assembled monolayers (SAMs) based on azobenzenes bearing different substituents at their para positions (Scheme 5). In the case of trans-1 SAMs or trans-2 SAMs on gold, the WCA of the surfaces decreased for 5º or 7º upon UV irradiation, respectively.[65] However, the dipole moment of cis-3 (2.77 D) was calculated to be lower than that of trans-3 (4.93 D) because of the electron withdrawing properties of the N=N moiety and the cyano group cancelled partially each other, leading to the unusual increase of the WCA of trans-3 SAMs after UV irradiation.
Unfortunately, the change in WCA of azobenzene monolayers on flat surfaces is typically in the order of 2-14º.\cite{66,67,68,69} Larger changes are required for the construction of photoswitchable surface with tailored properties. It was already discussed in section 1.3.1 that the surface wettability variation could be enhanced by the introduction of surface roughness. Cho et al. developed an organic-inorganic hybrid deposition technique with layer-by-layer porous structures on silicon wafer terminated with amine functional groups. These amines were further functionalized via covalently attachment of azobenzenes bearing a trifluoromethyl (CF$_3$) group at the para position.\cite{70,71} Increasing the number of deposition cycles enhances the surface roughness and nanoporosity, hence the WCA difference of the azobenzene film before and after UV irradiation could be increased from 5º for the flat surface to 150º for the surface after 9 deposition cycles. This is the first photoresponsive surface based on azobenzene which could be switched from superhydrophobic (WCA=152º) to superhydrophilic (WCA<5º).

Similarly, an azobenzene polyelectolyte 4 for fabricating organic films through electrostatic interaction on a silicon substrate was reported by Jiang et al. (Scheme 6, left).\cite{72} A WCA change of 66º of the 4 monolayer after UV irradiation was achieved by introducing patterned square pillars on flat silicon substrate.
through photolithography (Scheme 6, right)\textsuperscript{[73]}; this difference is 33 times larger than the difference of a flat silicon substrate covered with the same polymeric 4 after irradiation (ΔWCA=2º). The amplification of WCA changes is attributed to the increased surface roughness by the micropillars on the patterned silicon substrates, and the trapped air in the microgrooves leading to a more hydrophobic surface (Cassie wetting, see section 1.3.1).\textsuperscript{[60]}

The effect of surface roughness was also examined by using SAMs of a photocontrollable molecular shuttle on the basis of an α-cyclodextrin/azobenzene (α-CD/AB) inclusion complex (Figure 5).\textsuperscript{[74]} The mixed monolayer of n-C\textsubscript{4}H\textsubscript{9}SH and the α-CD/trans-AB complex was assembled on a rough gold surface with the hydrophilic α-CD ring exposed to the interface (Figure 5 upper left, WCA= 70º). Upon UV irradiation, the α-CD cavity cannot include the bulky cis-AB anymore due to the mismatch between the host and guest in shape, forcing the hydrophilic α-CD to be hidden from the interface by the cis-AB (Figure 5 lower left), hence an increase of WCA from 70º to 120º was observed. It should be noted that the WCA change of the same mixed-monolayer on flat gold surface upon UV irradiation is only ~2º, demonstrating the importance of surface roughness in constructing photoresponsive surface with larger wettability change.

**Figure 5** Schematic representation of an α-cyclodextrin/azobenzene inclusion complex (left, green cylinder = α-CD) and the corresponding change in WCA (right). Adapted from Ref. \textsuperscript{[44]}.

In a similar approach photocontrollable SAMs consisting of an calix[4]arene/trans-5 inclusion complex grafted on rough silicon wafer by click chemistry was reported by Li et al. (Scheme 7, left).\textsuperscript{[75]} The N atoms of the dimethylamino groups are electronegative and have affinity for the carboxylic acid group of the trans-5. Upon trans→cis photoisomerization by irradiation with UV light, cis-5 was released from the calix[4]arene cavity (Scheme 7, right) due to the geometrical mismatch between the host and guest, caused the exposure of the
hydrophobic dimethylamino groups to the interface and hence an increase of WCA from 24° to 140°. The micro/nanostructured silicon surface again played an important role in the amplification of the WCA variation.

The first example of macroscopic movement of liquid droplet on a flat solid surface modified with an azobenzene monolayer was reported by Ichimura et al. who used aminosilylated silica substrated functionalized with azobenzene-containing calix[4]resocrinarene (Figure 6a).[67,76]

The calix[4]resocrinarene moiety dictates the orientation of the azobenzenes and increase the space between the azobenzenes in the surface-bound assembly sufficiently to ensure efficient photoisomerization of the photochromic units. UV irradiation (365 nm) of the trans-6 functionalized surface resulted in formation of the cis-6 which has a larger dipole moment, hence the spreading of the droplet was observed after trans→cis photoisomerization. Macroscopic movement of the droplet was achieved by exposing the cis-6 riched surface to blue light (436 nm) in a spatially controlled manner with a gradient of intensity (Figure 6b) to create gradients in surface free energy, which results in a directional transport of a liquid droplet at a constant velocity (35 µm/s for olive oil). This system has the advantage that the direction and the speed of the movement is tunable by varying the direction and steepness of the gradient in light intensity.

Scheme 7 Reversible switching of the host-guest system of calix[4]arene and azobenzenes.
Figure 6 (a) A calix[4]resorcinarene derivative with azobenzene units. (b) Light-induced motion of an olive oil droplet on silica substrate decorated with cis-6. The droplet on the cis-rich surface moves in the direction of the higher surface energy area by exposure to blue light with a gradient in intensity. Adapted from Ref. [44].

1.3.3 Dithienylethene based thin films

There are two major approaches to control surface wettability: one is to change the polarity of the surface with photochromic azobenzene and spiropyran units as described in the previous sections. The other is to change the morphology of the surface, since the increase in surface roughness results in an enhancement in surface hydrophobicity (see section 1.3.1 and 1.3.2).

Irie et al. reported surface morphology changes upon UV irradiation due to the formation of needle-shape crystals on a glass substrate coated with dithienylethenes in the ring-open form (Figure 7a). The WCA of this dithienylethenes film was initially 120°, upon UV irradiation (254 nm) the color of the film turned deep blue indicating photocyclization of the dithienylethene from the ring-opened form to the ring-closed form, and the surface became superhydrophobic (WCA = 163°). SEM images showed that the surface was covered with microfibrils after UV irradiation (diameter around 1 µm; Figure DTE 1b). Upon irradiation of the substrate with visible light (λ > 500 nm), the surface became flat (Figure DTE 1c) and its initial WCA of 120° was recovered.
Figure 7 SEM images of the dithienylethene coated glass (Scale bar: 10 µm). (a) Before UV irradiation; (b) After UV irradiation and keeping the surface in dark for 24 h; (c) After irradiation with visible light and keeping the surface in dark for 24 h. Adapted from Ref. [77].

However, in Irie’s system, the change in WCA is relatively small (120° ↔ 163°) and it took 24 h to form the rough surface by the formation of the fine fibril structures. To generate a larger WCA change, Uchida et al. designed new surface coated with dithienylethene derivative 7o with a SO₂ group on one of the thiophenes to enhance the polarity of the surfaces (Scheme 8). In this system, the superhydrophobic rough surface (WCA > 150°) could be converted to hydrophilic flat surface (WCA < 90°) upon UV irradiation in 1 h due to the melting of the microcrystalline 7o. This flat surface could be switched back to its original morphology by irradiation with visible light. The faster change in surface morphology in combination with larger change in WCA makes this system suitable for application in lithography and in biological environment.[78]

Scheme 8 Molecular structure of the asymmetric diarylenes.
1.3.4 Rotaxane-functionalized surface

Macroscopic liquid transport by surface functionalized with photoresponsive rotaxanes were reported by Leigh, Rudolf, and Zerbetto et al. They designed a rotaxane consists of a macrocycle in a shuttle with perfluoroethyl segment on one side and a fumaramide moiety on the other (Scheme 9). The pyridine containing rotaxanes could be grafted to a monolayer of \( n\text{-C}_{10}\text{H}_{20}\text{CO}_2\text{H} \) on gold film by physical adsorption.\(^{[25,80]}\)

![Scheme 9 Molecular shuttle based on rotaxanes.](image)

In the \( E \)-isomer of the rotaxane, the macrocycle is positioned at the fumaramide station, hence the perfluoroethyl chain at the other end of the thread is exposed to the surface, making the interface hydrophobic. Upon UV irradiation, the fumaramide (which has higher affinity to the macrocycle) is converted to maleamide (which has lower affinity to the macrocycle), as a consequence, the macrocycle ring moves to the perfluoroethyl segment of the thread (\( Z \)-isomer). The relocation of the macrocycle cause the shielding effect of the perfluoroethyl chain, hence the interface could be changed from hydrophobic to less hydrophobic.

Macroscopic liquid transport was achieved by UV irradiation on one side of a \( \text{CH}_2\text{I}_2 \) droplet (1.25 \( \mu \)L) on the surface grafted with \( E \)-isomers to create a surface energy gradient across the length of the droplet (Figure 8, a), resulting in millimeter-scale directional transport of the droplet at a mean speed of \( \sim 1 \mu \text{m s}^{-1} \) (Figure 8, a→d). Zerbetto et al. further demonstrated that this molecular shuttle could do macroscopic work against gravity by moving a droplet up a 12º incline (Figure 8, e→h). This technique may prove useful for transporting chemicals in lab-on-a-chip environment, or carrying out chemical reactions without vessels by
Light-driven directional transport of droplet across the rotaxane-functionalized surface, both flat (a→d) and up a 12° incline (e→h). Adapted from Ref. [79]
1.4 Potential of molecular motors in control of surface wettability

1.4.1 Light-driven molecular motors

Molecular motors are a unique group of photoresponsive organic molecules that are able to convert light energy into repetitive unidirectional rotary motion which is controlled by the stereogenic center in the rotor moiety.\textsuperscript{[7,81]}

The full 360° unidirectional rotary cycle occurs through a four-step switching cycle. These steps involve two energetically uphill photochemical isomerization steps (Scheme 10, step 1 and 3), each followed by an energetically downhill and irreversible thermal isomerization step (Scheme 10, step 2 and 4), resulting in a full 360° rotation of the rotor respected to the relative stator. The irreversibility of the thermal isomerization steps is the key to the unidirectionality of the rotary cycle.

\begin{scheme}
\centering

\begin{tikzpicture}
\node at (0,0) {\textbf{Rotor}};
\node at (0,-1.5) {\textbf{Axle}};
\node at (0,-3) {\textbf{Stator}};

\node at (2,0) {\textbf{MeO}};
\node at (2,-1.5) {\textbf{MeO}};
\node at (2,-3) {\textbf{MeO}};

\node at (3.5,0) {\textbf{h} \nu (M)\textbf{ stable-trans 8}};
\node at (3.5,-1.5) {\textbf{h} \nu (P)\textbf{ unstable-cis 8}};
\node at (3.5,-3) {\textbf{h} \nu (M)\textbf{ stable-cis 8}};
\node at (3.5,-4.5) {\textbf{h} \nu (P)\textbf{ unstable-trans 8}};

\draw[->] (0,0) -- (2,0);
\draw[->] (0,-1.5) -- (2,-1.5);
\draw[->] (0,-3) -- (2,-3);

\draw[->] (3.5,0) -- (3.5,-1.5);
\draw[->] (3.5,-1.5) -- (3.5,-3);
\draw[->] (3.5,-3) -- (3.5,-4.5);
\draw[->] (3.5,-4.5) -- (3.5,0);

\node at (2.25,-2) {\textbf{\(\Delta\)}};
\node at (3.5,-2) {\textbf{\(\Delta\)}};

\end{tikzpicture}
\end{scheme}

\textbf{Scheme 10} Photochemical and thermal isomerization processes of molecular motors.
Since the rate of the photoisomerization steps (Scheme 10, step 1 and 3) was found to be much higher (on picosecond timescale)\textsuperscript{[82]} than the thermal isomerization steps (Scheme 10, step 2 and 4), the latter is considered as the rate-determining step of the rotary cycle. Our group have designed, synthesized, and studied a series of molecular motors leading to a better understanding how different substituents and ring sizes influence the rotation rate (Scheme 11).\textsuperscript{[83]}

\begin{align*}
\text{Molecular motors} & \quad \text{(Scheme 11)} \\
& \quad \text{Representative molecular motors and their rotation rates expressed in terms of the half-life (t}_{1/2}\text{) of the thermal isomerization step at room temperature (rt).}
\end{align*}

Molecular motors are promising candidates in photochemically-driven systems as multi-stage switches. It has already been shown that molecular motors can be used to perform various tasks, such as propelling single molecules in a controlled manner,\textsuperscript{[15]} inducing the rotation of liquid crystal’s surface texture or a micro-object,\textsuperscript{[84]} and controlling the chiral space in which a catalytic reaction occurs.\textsuperscript{[85]}

1.4.2 From relative to absolute rotation

A key challenge in developing photo-driven systems based on molecular motors is to exploit their collective rotary motion in order to interact with external, micro- or macro-objects in a dynamic manner. However, the rotary motion of molecular motors is overwhelmed by Brownian motion while the molecules are in solution.
Confining molecular motors to surfaces could inhibit Brownian motion and hence the relative rotation of one part of the molecule with respect to the other could be converted to absolute rotation of the rotor relative to the surface.

When molecular motors are attached to the surface, two kinds of orientations can be envisioned: azimuthal and altitudinal (Figure 9). In the azimuthal orientation the axis of rotation is perpendicular to the surface, while in the altitudinal orientation it is parallel to the surface.

Figure 9 A schematic view of azimuthal (left) and altitudinal (right) orientations. Reproduced from Ref. [86].

1.4.3 Azimuthal molecular motors on surfaces

The first example of unidirectional rotary motion on a surface using azimuthal molecular motors was reported by van Delden et al. In this design, molecular motors 18 with two thiol-terminated legs were attached to gold nanoparticles (NPs) by sulfur-gold bonds (Scheme 12). The two attachment points prevent the uncontrolled thermal rotation of the whole system with respect to the surface and hence upon UV irradiation the relative rotation of the rotor with respect to the stator (Scheme 10) can be converted to the rotation of the rotor relative to the surface of the NPs.

The self-assembly on gold NPs facilitates monitoring the repetitive rotary process of the motors using standard solution analysis techniques, including UV/vis absorption, circular dichroism (CD), and ^1^H NMR spectroscopies. The half-life ($t_{1/2}$) of the thermal isomerization step from ($P$) unstable 18 to ($M$) stable 18 (Scheme 12, step 2 and 4) while anchored on the gold NPs was $12 \times 10^3$ s at rt, which is almost double than that of its parent motor ($5.6 \times 10^3$ s at rt). The longer $t_{1/2}$ indicates that the rotation speed of the surface-bound motor slows down and is attributed to the reduction in degree of freedom when motors are attached to the
surface. Although the rotary motion of the motors is preserved while grafted to the gold NPs, these NPs are still in the solution phase, hence the rotary motion of the motor is still overwhelmed by Brownian motion via rotational and translational motion, making it challenging to harness work from this system.

Scheme 12 Full rotary cycle of molecular motor 18 anchored on gold nanoparticles.

The uncontrolled Brownian motion was later overcome by immobilizing motors 19 on quartz\textsuperscript{[89]} or 20 on gold films\textsuperscript{[90]} (Scheme 13). The attachment of azimuthal motor 19 to quartz through two attachment points was verified by X-ray photoelectron spectroscopy (XPS). By using CD spectroscopy, the photochemical and thermal behavior of the motors on the quartz and gold films were correlated to
their solution analogues and is consistent with unidirectional rotary motion, indicating that the rotary motion is preserved while attached to solid substrates.\(^1\)

\[\begin{align*}
\text{Scheme 13} & \quad \text{Azimuthal molecular motors on amine-functionalized quartz (a) and gold films (b).}
\end{align*}\]

To harness the rotary motion of the molecular motors, two key issues should be taken into account: (a) Their rotary speed should be fast enough to compete with the Brownian motion; (b) To limit the positional and orientational degrees of freedom of the motors, they need to be immobilized on macroscopic surfaces. These two issues were addressed by grafting a monolayer of ultrafast motors on solid surfaces. In this design, an ultrafast molecular motor 22 with \(t_{1/2}\) of 38 ns at rt (measured by ns-pulsed laser transient absorption spectroscopy)\(^{91,92}\) was attached to azide-functionalized quartz by a click approach (Scheme 14).\(^{93}\)

The quartz surface was first functionalized with a monolayer of azides, followed by immersing this azide substrate in a 1mM solution of 22 in the presence of CuSO\(_4\)•5 H\(_2\)O and sodium ascorbate in DMF, affording stable 22. The presence of the motor 22 on the surface was confirmed by UV/vis absorption spectroscopy, WCA measurement, attenuated total reflection infrared spectroscopy (ATR-IR), and ellipsometry. After reaction, the UV/vis absorption spectrum of stable 22 showed the characteristic absorption profile of the motors, the WCA decreased from 78° to 65°, the IR spectrum showed the disappearance of the band corresponding to the azide, and the thickness of the organic layer increased by

\[\begin{align*}
\text{EtPr}_{2}N \quad \text{Cl(O)Cl} \\
\text{NH}_2 \quad \text{Cl(O)Cl} \\
\text{Si} \quad \text{Si} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{S} \\
\text{Gold} \\
\text{n n} \\
\text{(M) stable 19} \\
\text{(M) stable 19} \\
\text{(M) stable 19} \\
\text{(M) stable 19} \\
\text{(M) stable 21} \\
\text{n = 9} \\
\text{n = 1}
\end{align*}\]

\(^1\) It should be noted that when motors are assembled too close to the gold surface (Scheme 13b, n=1), quenching of the photoinduced excited state of the motors by the gold substrate may occur, preventing motors from functioning properly.
0.8 nm as determined by ellipsometry. These results all indicate that the ultrafast motor 22 was attached to the azide-functionalized quartz successfully.

Scheme 14 Grafting of the ultrafast motor 22 to azide-functionalized quartz through a click reaction.

It should be noted that immersion of an unmodified quartz slide in the solution of 22 or immersion of an azide-functionalized quartz in a solution of 22 without CuSO\textsubscript{4}•5 H\textsubscript{2}O did not give the characteristic UV/vis signal of motor 22, indicating that the Cu(I) catalyst is essential for the interfacial catalytic azide-alkyne cycloaddition. This represents the fastest molecular motor based on overcrowded alkenes that has so far been immobilized on a surface.

1.4.4 Altitudinal molecular motors on surfaces

Although the assembly of azimuthal molecular motors on a variety of surfaces is well-developed over the past decade, molecular motors rotating in an altitudinal orientation relative to the surface are expected to have greater potential for the construction of photo-switchable surfaces. It is easy to envision that the surface accessibility of a functional group on the rotor of the altitudinal motors could be modulated in a cyclic fashion.

The first example of rotary motion on surfaces based on an altitudinal molecular motor was reported by London and Carroll et al.\textsuperscript{[94,95]} In this design, a click approach was used to attach dialkyn motor 23 to an azide-functionalized surface by Cu(I)-catalyzed azide-alkyne cycloaddition (Scheme 15). The motor monolayers were characterized by a combination of UV/vis absorption and IR
spectroscopies, ellipsometry, WCA measurement, and XPS as described in the previous section. These measurements indicated that the motors were anchored on the surface successfully and the rotary motion of the surface-bound molecules is preserved. Despite the promise of the current design of altitudinal motors in powering surface-bound nanomachinery, the rotary motion of the surface-bound motors was found to be obstructed by intermolecular interaction when motors 23 are confined in crowded environments compared to solution. This issue was later addressed by designing a tripodal molecular motor with a bulky stator for surface attachment which could provide sufficient free volume for the isomerization steps of the surface-bound motors, as will be discussed in Chapter 3.

Scheme 15 Attaching dialkyne motor 23 to azide-functionalized quartz through a click approach.

The assembly of stimuli-responsive molecules on silicon-based surfaces is highly desirable because of their relevance to molecular electronic device, relative low price and thermal, chemical, and mechanical stabilities. London et al. designed a new approach to assemble molecular motors directly to quartz, silicon wafers, and mica without prior activation of these surfaces with amine- or azide-functional groups, as described in section 1.4.3 (Scheme 16).
In this approach, the molecular motors were functionalized with two triethoxysilane units at their “legs” for attachment to Si-OH terminated surface (quartz and silicon wafer cleaned with piranha solution). The motors attached to these surfaces were found to undergo photochemical and thermal isomerization similar to their solution analogues by UV/vis absorption and CD spectroscopies.

The direct attachment of motor 24 on mica, an atomically flat surface, is of particular interest since it facilitates AFM studies of the photoinduced morphology changes of the motor based films (Figure 10). Such morphological changes have great potential for inducing changes in surface wettability as described in section 1.3.3.

**Figure 10** AFM images of motor films on mica: (a) Sample before UV irradiation; (b) Sample after irradiation; (c) Sample after standing in dark overnight. Adapted from Ref. [97].
Chapter 1

1.4.5 Conclusions

A key challenge in developing surface-bound devices based on molecular motors is to exploit their collective motion for interacting with an external species in a dynamic manner. One way to demonstrate that the collective rotary motion of a surface-bound layer of oriented motors can influence interactions with an overlayer material is to monitor the contact angle of a liquid on top of the motor monolayer. To date, light-driven rotary molecular motor based surfaces that can induce changes in surface wettability upon irradiation have not been reported yet. The unique features that molecular motors are able to undergo controlled unidirectional rotary motion while attached to a surface in either an azimuthal or an altitudinal orientation, a wide range of rates at which they can rotate, a variety of surfaces to which they can be attached, and the potential to induce surface morphological changes make molecular motors attractive candidates for the dynamic modulation of surface properties and inducing macroscopic motion by harnessing collective changes in their molecular structure in surface bound assemblies.

1.5 Aim and outline of this thesis

The proper assembly of light-driven molecular motors on surfaces while retaining their rotary motion is particularly challenging and of great importance for harnessing their collective motion to perform work. To avoid interference effects, orientation with respect to surface, mode of attachment (number of legs), distance from the surface, rigidity of anchoring groups, and packing density of the rotor moieties are all basic issues to be considered and addressed for the successful construction of new surface-bound systems based on molecular motors for dynamic nanoscale applications.

In Chapter 2, the first concept of surface wettability control using light-driven molecular motors is demonstrated. In this design, a surface functionalized with cis or trans isomers of altitudinal motor with a hydrophobic chain on the rotor (Scheme 15, R= C₄F₉) shows a difference of 12° in WCA between the cis and trans isomers. However, once the motors are assembled on the surface, the wettability cannot be modulated by UV irradiation.

In Chapter 3, the design, preparation, and characterization of tripodal molecular motors for surface wettability control is described. The design comprises
a molecular motor with a hydrophobic perfluorobutyl chain on the rotor and a tripodal stator containing thiol groups for self-assembly on gold. The bulky stator dictates the orientation and increases the spacing between the rotors of the surface-bound motors sufficiently to facilitate unobstructed rotary motion. This is the first example of dynamic wettability control of solid surfaces using molecular motors decorated with a hydrophobic functional group on the rotor part.

In Chapter 4, the synthesis and photochemistry of novel molecular switches and motors bearing tetrapodal anchoring units are described. The anchoring units consist of anthracene molecules with four “legs” that are terminated with functional groups appropriate for surface assembly. A facile Diels-Alder reaction under mild conditions allows for the attachment of molecular switches and motors to the anthracene anchoring units in high yield. Studies on the photochemical and/or thermal isomerization processes of these tetrapodal molecular switches and motors are included, showing that their dynamic properties are not affected. The tetrapodal system provides an excellent platform for surface assembly of photoresponsive molecules with high control over anchoring at the surfaces.

In Chapter 5, molecular motors containing multivalent carboxylic acid groups on the stator for surface attachment is described. The acids allow for the motors to be attached to amine-coated surface without prior activation of the acid groups. Thermal isomerization of tetravalently attached motors was not inhibited considerably by surface immobilization; however, bivalently attached motors showed a large reduction in the speed of thermal isomerization, demonstrating how subtle differences in molecular structure can considerably impact dynamic processes in nanoscale systems.

With these studies we have made major steps in the design of surface assembled molecular motors and elucidated how dynamic behavior can be fully retained in surface-bound systems. The work described in this thesis sets the stage for the control of various functions using molecular motors including the control of interaction with surface adsorbates while it also provides the stepping stone to detailed studies of single motor rotation.
1.6 References


[83] For the half-lives of the thermal isomerization step of molecular motors, see: (a) **8, 9, 10, 14**, and **15**: Koumura, N.; Geertsema, E. M.; van Gelder, M. B.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2002**, *124*, 5037–5051. (b) **11**: Vicario, J.; Meetsma, A.; Feringa, B. L. *Chem. Commun.* **2005**, 5910. (c) **12**: ...


Chapter 1

