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

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Dedicated to the memory of Professor Nicholas J. Turro

Abstract: We report the synthesis of altitudinal molecular motors that contain functional groups in their rotor part. In an approach to achieve dynamic control over the properties of solid surfaces, a hydrophobic perfluorobutyl chain and a relatively hydrophilic cyano group were introduced to the rotor part of the motors. Molecular motors were attached to quartz surfaces by using interfacial 1,3-dipolar cycloadditions. To test the effect of the functional groups on the rotary motion, photochemical and thermal isomerization studies of the motors were performed both in solution and when attached to the surface. We found that the substituents have no significant effect on the thermal and photochemical processes, and the functionalized motors preserved their rotary function both in solution and on a quartz surface. Preliminary results on the influence of the functional groups on surface wettability are also described.

Keywords: molecular devices · nanotechnology · photochemistry · surface chemistry · wettability

Introduction

Control of the assembly and arrangement of molecules[1] on surfaces allows for interfaces with tailored properties to be created. Modifications of surfaces with self-assembled monolayers[2] (SAMs) provide opportunities to create interfaces that exhibit various properties including hydrophilicity/hydrophobicity,[3–6] conductance,[7,8] catalytic activity,[9,10] and chirality.[11–13] Amongst SAM-forming molecules, those that can switch reversibly between distinct geometrical forms accompanied with changes in physical properties such as dipole moment or conductance are particularly interesting.[14–16] Such reversible changes in chemical and physical properties facilitates the fabrication of multifunctional and dynamic interfaces that allow for responsive behavior by reversible switching from one desired property to another.

Azobenzenes and spiropyrans have been widely used to reversibly modulate surface free energy by light.[14–16] Azobenzenes can undergo *trans→cis* photoisomerization, which induces a change in dipole moment, which in turn determines the hydrophilic and hydrophobic nature of the isomers.[17] Spiropyrans can be switched photochemically between a relatively hydrophobic spirocyclic isomer and a hydrophilic zwitterionic merocyanine isomer.[18] Given the inherent changes in polarity that accompany structural changes, azobenzenes and spiropyrans can affect surface free energy in monolayer assemblies[19,20] without an additional functional group being required to ensure sufficient polarity change. Nevertheless, additional functional groups[20–22] and surface pretreatment[23] can enhance the effect of isomerization.

Molecular rotary motors based on overcrowded alkenes[24] are a unique class of compounds that can undergo repetitive unidirectional rotary motion upon irradiation with UV light. In a surface-bound ensemble of rotary motors, two types of rotary motion can be distinguished in terms of orientation: azimuthal[25–27] and altitudinal[28,29] (Figure 1). In comparison

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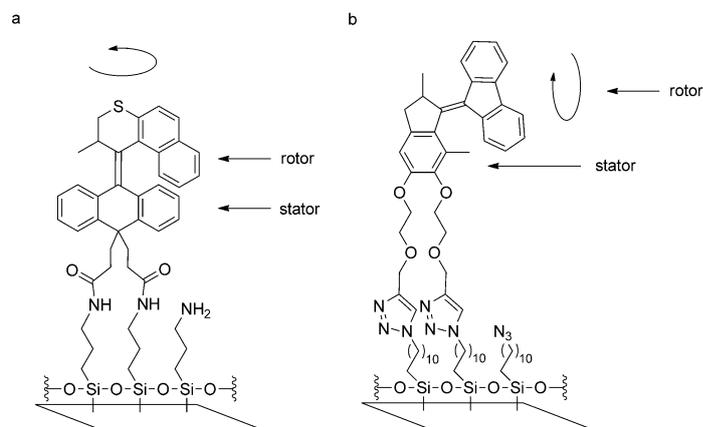
Figure 1. a) Azimuthal and b) altitudinal rotary motors. To exploit the rotary motion, the introduction of functional groups on the rotor part is required.

to azimuthal rotation, altitudinal rotary motion is expected to allow for the surface accessibility of functional groups on the rotor to be modulated in a cyclic fashion.
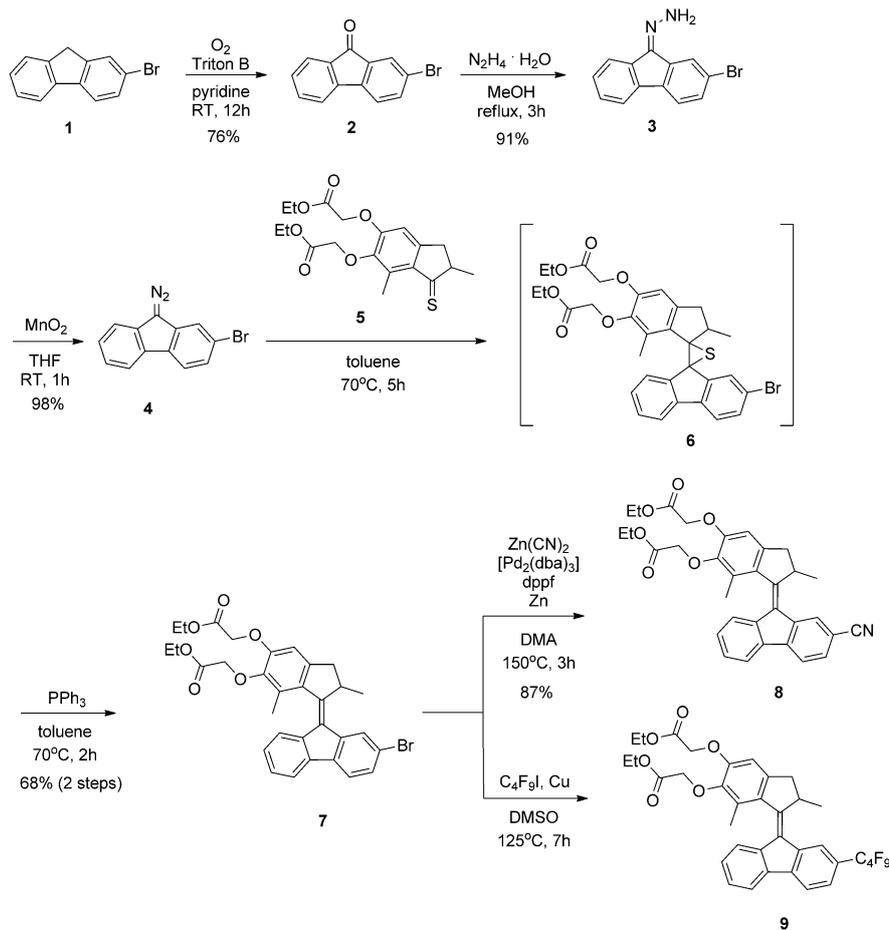
Relative to azobenzenes and spiropyrans, altitudinal motors that contain symmetric rotor units do not provide a sufficient change in polarity upon rotation that could affect macroscopic surface properties. To develop rotary motor-based interfaces that undergo cyclic changes in polarity, functional groups have to be introduced to the rotor part.

Previously we reported that interfacial 1,3-dipolar cycloaddition was found to be a reliable method that allows for the attachment of molecular motors to solid substrates.[28, 29] Here we describe the synthesis of molecular motors suitable for surface attachment that contain functional groups in the rotor part. To test the effect of the functional groups on the rotary motion, photochemical and thermal isomerization studies were performed in solution. Surface attachment in altitudinal orientation and the isomerization process of surface-bound motors are presented. Preliminary results on the influence of the functional groups on surface wettability are shown.

Scheme 1. Synthesis of a bromo-substituted molecular motor and the introduction of the cyano and perfluorobutyl substituents.

Results and Discussion

Synthesis: To attach different functional groups to the rotor part of the motor, a brominated derivative of 9-fluorenone was prepared through the oxidation of 2-bromofluorene (**1**) to 2-bromo-9-fluorenone (**2**). Fluorenone **2** was converted to the corresponding hydrazone **3** by heating at reflux in MeOH in the presence of hydrazine monohydrate followed by oxidation to the diazo derivative **4** with MnO_2 in THF (Scheme 1). The product was used in the subsequent diazo–thioketone coupling step without further purification.

The Barton–Kellogg coupling reaction[30, 31] between the upper-half thioketone **5** and the lower-half diazo compound **4** was performed in toluene at 70 °C for 5 h (Scheme 1). The formation of the corresponding episulfide **6** was followed by ^{1}H NMR spectroscopy as a shift of the upper-half aromatic proton from $\delta = 6.66$ ppm in the thioketone **5** to $\delta = 6.35$ and

6.37 ppm in the *cis/trans* isomers of the episulfide **6** in CDCl$_3$. Addition of PPh$_3$ (2 equiv) to the reaction mixture followed by an additional 2 h stirring at 70 °C provided the overcrowded alkene **7** in 68 % yield as a mixture of *cis/trans* isomers. Although one of the isomers (*trans*-**7**) of the motor could be obtained as a single isomer by precipitation from Et$_2$O at this stage, the mixture of the isomers was used in the next step.

The cyano group, as a relatively hydrophilic substituent, was introduced by means of palladium-catalyzed cyanation of bromo motor **7** by using the protocol of Jin and Confalone[32] (Scheme 1). This methodology has already been applied successfully to the introduction of the cyano functional group to molecular motors.[33] As expected, the reaction gave product **8** in high yield without affecting the other functional groups present in the molecule.

A possible way to introduce hydrophobicity into the motor is to functionalize the rotor part with a perfluoroalkyl chain. Copper-mediated cross-coupling reactions between aryl halides and perfluoroalkyl iodides have been used successfully to synthesize perfluoroalkylated aryl compounds.[34, 35] By using this approach, coupling bromo motor **7** with perfluorobutyl iodide gave compound **9** without the

observation of any degradation of the motor (Scheme 1). A drawback of this functionalization method is, however, that it is not possible to completely separate the unreacted starting material **7** from the perfluoroalkylated product **9**.

An alternative approach to introduce the perfluorobutyl chain to the rotor part is the coupling between perfluorobutyl iodide and the bromo-functionalized lower half of **2** (Scheme 2). To this end bromoketone **2** was subjected to perfluoroalkylation under the same conditions as bromo motor **7**, and the desired product **10** could be obtained in 72 % yield. Ketone **10** was subsequently transformed into the corresponding hydrazone with hydrazine monohydrate, and compound **11** was obtained as a mixture of *cis* and *trans* isomers. The preparation of hydrazone **11** requires lower

temperatures than the hydrazone derived from symmetric 9-fluorenone or **2**. Under reflux conditions in MeOH, the ketone is expected to undergo Wolff–Kishner reduction to yield the corresponding fluorene.[36] Hydrazone **11** was converted to the diazo derivative by oxidation with MnO$_2$ in THF to provide 2-perfluorobutyl-9-diazofluorene (**12**), which was used immediately in the following diazo–thioketone coupling reaction.

The Barton–Kellogg coupling was performed similarly as in the previous case. The upper half thioketone **5** and the lower half diazo compound **12** were heated at 75 °C in toluene for 3 h. After most of the thioketone was converted to episulfide **13** (the absorption of the upper-half aromatic protons of the isomers of **13** appear at $\delta = 6.34$ and 6.39 ppm in CDCl$_3$), PPh$_3$ (2 equiv) was added to the mixture, followed by stirring at 75 °C for an additional 2 h to yield motor **9** as a mixture of *cis/trans* isomers (1.4:1) in 70 % yield after purification by column chromatography.

To introduce terminal alkyne groups to the motors that are necessary for surface attachment by means of 1,3-dipolar cycloadditions, the esters in **8** and **9** were reduced and the corresponding alcohols **14** and **15** were alkylated with propargyl bromide (Scheme 3). The reduction of the ester groups was carried out with LiBH$_4$ in THF. Separation of the two isomers of compound **15** was possible at this stage by column chromatography over silica gel (Et$_2$O) to yield *cis*-**15** and *trans*-**15** in 24 and 34 % yield, respectively. Next, the two isomers of diol **15** and the *cis/trans* mixture of diol **14** were alkylated with propargyl bromide in the presence of NaH in THF. The *cis* and *trans* isomers of alkene **16** could be separated by column chromatography over silica by using a toluene/Et$_2$O (20:1) eluent mixture, so the *cis* and *trans* isomers of compounds **16** and **17** were obtained in 31, 47, 64, and 78 % yields, respectively. The *cis* and *trans* isomers of diol **15** and dialkyne **16** were assigned by comparison of
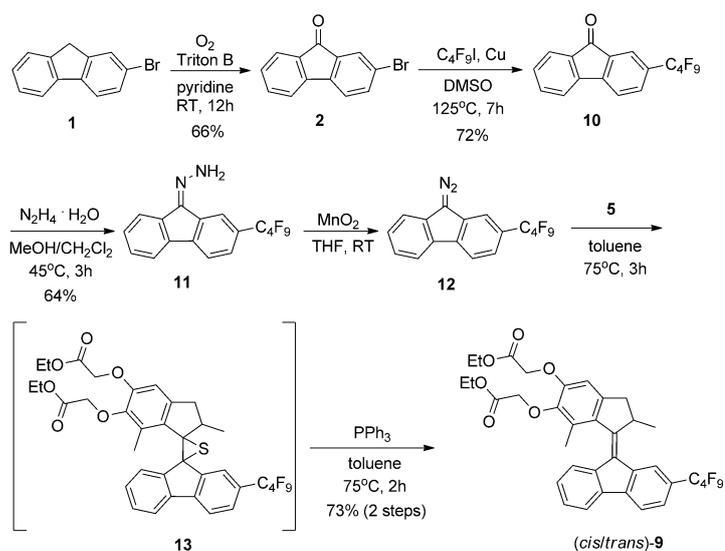

Scheme 2. Alternative synthesis route towards perfluorobutyl-substituted molecular motor **9**.
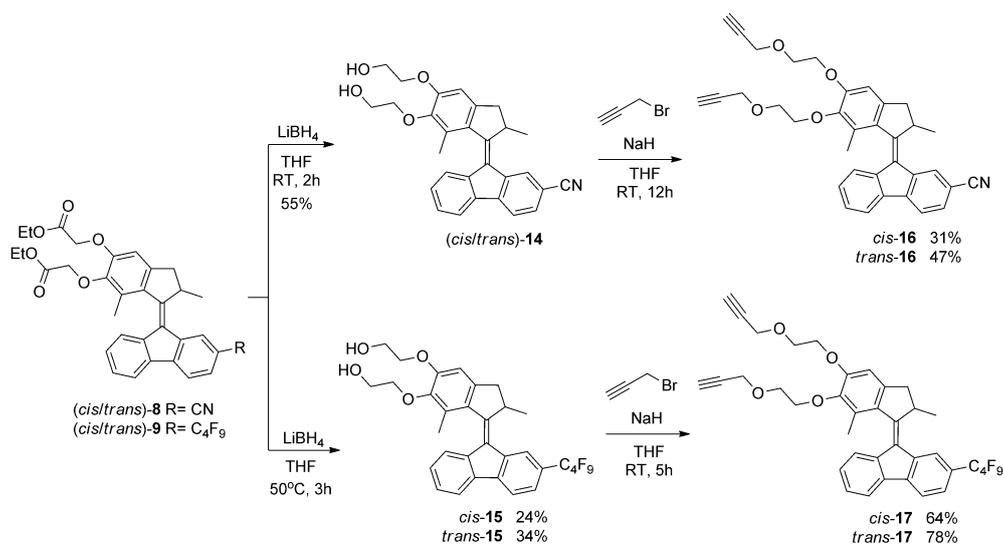
Scheme 3. Introduction of terminal alkynes onto substituted motors **8** and **9** that allows for controlled surface modification by means of interfacial 1,3-dipolar cycloadditions.

their ^{1}H NMR spectra (Figure S1 in the Supporting Information)[37] with that of previously reported structurally related molecular motors.[38–41]

Characterization of the rotary cycle: To show that **16** and **17** operate as molecular motors,[24] photochemical and thermal isomerization studies were carried out in solution by using low-temperature UV/Vis and ^{1}H NMR spectroscopy. The UV/Vis spectra of a sample of the stable forms of cis-**16** and trans-**16** in MeOH at −20 °C show absorption bands centered at 395 nm, whereas under identical conditions the major absorption band of the cis and trans isomers of alkene **17** are centered at 388 nm (Schemes 4 and 5, solid line).
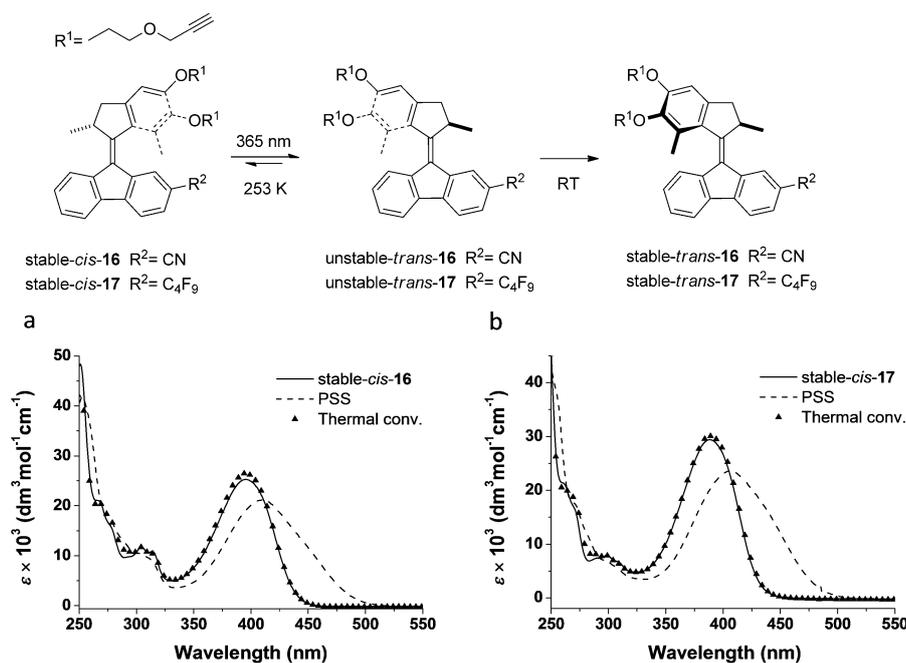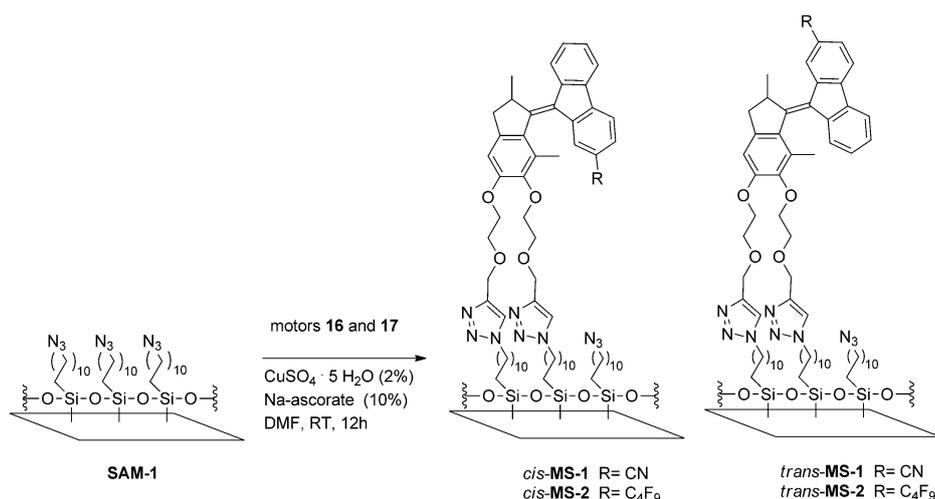

Scheme 4. Photochemical and thermal isomerization studies of stable-cis-**16** and stable-cis-**17**. a) UV/Vis spectra of stable-cis-**16** (solid line), the PSS mixture of stable-cis-**16** and unstable-trans-**16** after irradiation at $\lambda_{max} = $ 365 nm (dashed line), and the mixture of stable-cis-**16** and stable-trans-**16** after thermal conversion upon standing at RT for 15 min (▲). b) UV/Vis spectra of stable-cis-**17** (solid line), the PSS mixture of stable-cis-**17** and unstable-trans-**17** after irradiation at $\lambda_{max} = $ 365 nm (dashed line), and the mixture of stable-cis-**17** and stable-trans-**17** after thermal conversion upon standing at RT for 15 min (▲).

Compared to the parent motor without substituents on the rotor part (major absorption band at 378 nm),[28] introduction of the substituents resulted in a slight redshift of the UV/Vis absorption. Such shifts have already been observed upon the introduction of electron-donating or electron-withdrawing groups to molecular motors,[33] azobenzenes, and stilbenes.[42–44] In the case of the cis- and trans-cyano-substituted motor **16**, the maxima of the major absorption band of the stable isomers in MeOH are more redshifted than those of the fluoroalkyl motors **17**. This shift is attributed to the stronger electron-withdrawing character of the cyano group than the perfluoroalkyl chain.[33]

Irradiation of a sample of stable forms of solutions of cis-**16** and cis-**17** and trans-**16** and trans-**17** in MeOH at −20 °C

with UV light ($\lambda_{max} = 365$ nm) led to a redshift and broadening of their UV/Vis absorptions, thus indicating the photochemically induced formation of the unstable isomers (Schemes 4 and 5, dashed lines). The shifted bands are centered at 412 and 405 nm for cis-**16** and cis-**17**, and 407 and 400 nm for trans-**16** and trans-**17**, respectively. During irradiation, clear isosbestic points were observed in all cases, thus indicating that the photochemical isomerization from the stable to unstable form proceeds cleanly. Samples were irradiated until no further changes were observed, thus indicating that the photostationary state had been reached. Allowing the solutions to warm to room temperature led to reversion to the original spectra consistent with thermal relaxation to the corresponding stable isomers (Schemes 4 and 5).

The thermal isomerization of unstable-cis-**16** and unstable-trans-**16** to the corresponding stable isomers was monitored by UV/Vis spectroscopy at 450 nm as a function of time at four different temperatures (253, 258, 263, and 268 K). From the first-order rate constants the Gibbs free energy of activation ($\Delta^\ddagger G°$) for the thermal helix inversion could be determined with the Eyring equation; they were calculated to be 82.2 kJ mol^{-1} for the unstable-cis-**16**→stable-cis-**16** and 82.5 kJ mol^{-1} for the unstable-trans-**16**→stable-trans-**16** process (Figure S2 in the Supporting Information).[37] By extrapolation of the kinetic data, half-lives ($t_{1/2}$) at RT of 50 and 57 s were calculated for the unstable-cis-**16**→stable-cis-**16** and unstable-trans-**16**→stable-trans-**16** processes, respectively. In the same manner the conversion of unstable-cis-**17** and unstable-trans-**17** to the corresponding stable isomers was monitored by UV/Vis spectroscopy at 440 nm as a function of time at different temperatures that ranged from 253 to 273 K. The Gibbs free energy of activation ($\Delta^\ddagger G°$) was calculated to be 83.3 kJ mol^{-1} for the unstable-cis-**17**→stable-cis-**17** and 84.0 kJ mol^{-1} for unstable-trans-**17**→stable-trans-**17** thermal conversions (Figure S3 in the Supporting Information).[37] By extrapolation of the kinetic data, half-lives ($t_{1/2}$) at RT of 81 and 102 s were calculated for the unstable-cis-**17**→stable-cis-**17** and unstable-trans-**17**→stable-trans-**17** processes, respectively. These values are similar to those obtained for structurally related motors,[38–41] thus indicating that the introduction of the functional groups does not have significant influence on the thermal isomerization steps.

Scheme 5. Photochemical and thermal isomerization studies of stable-*trans*-**16** and stable-*trans*-**17**. a) UV/Vis spectra of stable-*trans*-**16** (solid line), the PSS mixture of stable-*trans*-**16** and unstable-*cis*-**16** (dashed line) after irradiation at $\lambda_{max} = 365$ nm, and the mixture of stable-*trans*-**16** and stable-*cis*-**16** (▲) after thermal conversion upon standing at RT for 15 min. b) UV/Vis spectra of stable-*trans*-**17** (solid line), the PSS mixture of stable-*trans*-**17** and unstable-*cis*-**17** after irradiation at $\lambda_{max} = 365$ nm (dashed line), and the mixture of stable-*trans*-**17** and stable-*cis*-**17** after thermal conversion upon standing at RT for 15 min (▲).

sible 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.[33] However, for definitive conclusions on the precise solvent effect further studies on the solvent dependence of the PSS composition of alkenes **17** should be performed. When the samples that contained the PSS mixtures were allowed to warm to RT for 30 min, the ^{1}H NMR spectra showed quantitative conversion of the unstable isomers to the corresponding stable isomers.

Surface attachment and characterization: Molecular motors **16** and **17** were attached to quartz surfaces through interfacial 1,3-dipolar cycloaddition reactions[45–47] as developed and described for molecular motors with a nonfunctionalized rotor part.[28, 29] It was expected that the functional groups would not interfere with the copper-catalyzed coupling reaction and that the functionalized motors would bind to quartz under identical reaction conditions to those reported previously.[28, 29] To attach the alkyne-terminated motors to quartz surfaces through interfacial 1,3-dipolar cycloadditions, an azide-terminated monolayer was prepared using 11-azidoundecyltrimethoxysilane[28, 29] (Scheme 6). Piranha-cleaned quartz slides were immersed in

To further characterize the unstable isomers and determine the composition of the photostationary state (PSS), low-temperature ^{1}H NMR spectroscopic measurements were performed. Irradiation ($\lambda_{max} = 365$ nm) of a sample of stable *cis* and *trans* isomers of **16** and **17** in CD_2Cl_2 at −55 °C resulted in the appearance of new absorptions in their ^{1}H NMR spectra.[37] The identity of the unstable isomers was evident from the downfield shift of the doublet absorptions of the stereogenic methyl groups of the stable forms (Table 1). These shifts are consistent with the conformation-

Table 1. Photostationary states (PSS) determined by ^{1}H NMR spectroscopy after irradiation at $\lambda = 365$ nm in CD_2Cl_2 at −55 °C.

Alkene	PSS$_{365\,nm}$ unstable/stable	^{1}H NMR absorptions of $(CH_3)_{ax} \rightarrow (CH_3)_{eq}$ [ppm]
cis-**16**	5:1	1.28→1.42
trans-**16**	3.5:1	1.29→1.45
cis-**17**	2.5:1	1.29→1.41
trans-**17**	2:1	1.29→1.46

al change of the stereogenic methyl substituents from the preferred pseudoaxial to the unfavored pseudoequatorial orientation upon photoisomerization. The relative integration of the absorptions of the stable and unstable isomers revealed similar PSS compositions for both compounds, with slightly less favorable values for alkenes **17** (Table 1). A pos-

a solution of azide **18** in cyclohexane/THF that contained a small amount of water and acid to hydrolyze the methoxysilane groups to silanol groups.[37] Quartz slides were immersed in the hydrolysis solution for 12 h, then rinsed by sonication in toluene, DMF, and MeOH (2 min in each solvent), and dried under a stream of argon. Typical water contact angles for **SAM-1** prepared by this method were (83 ±

Scheme 6. Assembly of an azide-terminated monolayer on quartz surface.

Scheme 7. Attachment of the *cis* and *trans* isomers of motors **16** and **17** to azide-functionalized quartz surfaces through a copper-catalyzed interfacial azide–alkyne cycloaddition reaction.

faces modified with *cis-* and *trans-***16** and -**17** (Figure 3 and Figures S4 and S5 in the Supporting Information).[37] Motor-modified surfaces *cis-***MS-1** and *trans-***MS-1** showed water contact angles of (67 ± 1) and $(60 \pm 1)°$, respectively. The contact angle for *cis-***MS-1** is the same as that obtained for the unsubstituted parent motor on quartz,[28] thus indicating that the cyano group does not change the surface energy considerably, probably due to its small size and comparable polarity to the hydrophilic ethylene glycol units beneath the motor.

In the case of *cis-***MS-2**, in which the perfluorobutyl chains are likely hidden from the interface, a contact angle of $(80 \pm 2)°$ was measured. For *trans-***MS-2**, in which the perfluorobutyl chains are exposed to the interface, a contact angle of $(92 \pm 1)°$ was obtained that is due to the hydrophobic character (low surface energy) of the fluoroalkyl chains. The effect of the substituent on the wettability of the surface is evident when compared to the motor with a symmetric rotor part, for which a water contact angle of $(67 \pm 2)°$ was measured.[28] The higher

$2)°$, which is in agreement with contact angles reported earlier for azide-functionalized surfaces.[28,29,48–50]

To test the effect of the substituents on the photochemical and wetting properties of the modified surface, both isomers of motors **16** and **17** were attached to quartz substrates (Scheme 7).

The UV/Vis spectra of the quartz substrates immersed in a solution of *cis-* and *trans-***16** and -**17** in DMF (1 mM) in the presence of copper catalyst showed the characteristic absorption of the motors, which indicates that the attachment was successful (Figure 2, solid line). The maxima of the major absorption band (centered at 399 nm for **MS-1** and 390 nm for **MS-2**) and the absorption profile are similar to that observed in MeOH solution. Irradiation of the functionalized slides at $\lambda_{max} = 365$ nm at $-5°C$ resulted in a moderate shift of the UV/Vis absorption (centered at 403 nm for unstable-**MS-1** and 394 nm for unstable-**MS-2**; Figure 2, dashed line) similar to that observed in MeOH, thus indicating the formation of the unstable form of the surface-bound motors. Upon leaving the sample overnight at room temperature, the UV/Vis absorption reversed, which is consistent with the thermal isomerization process (Figure 2).

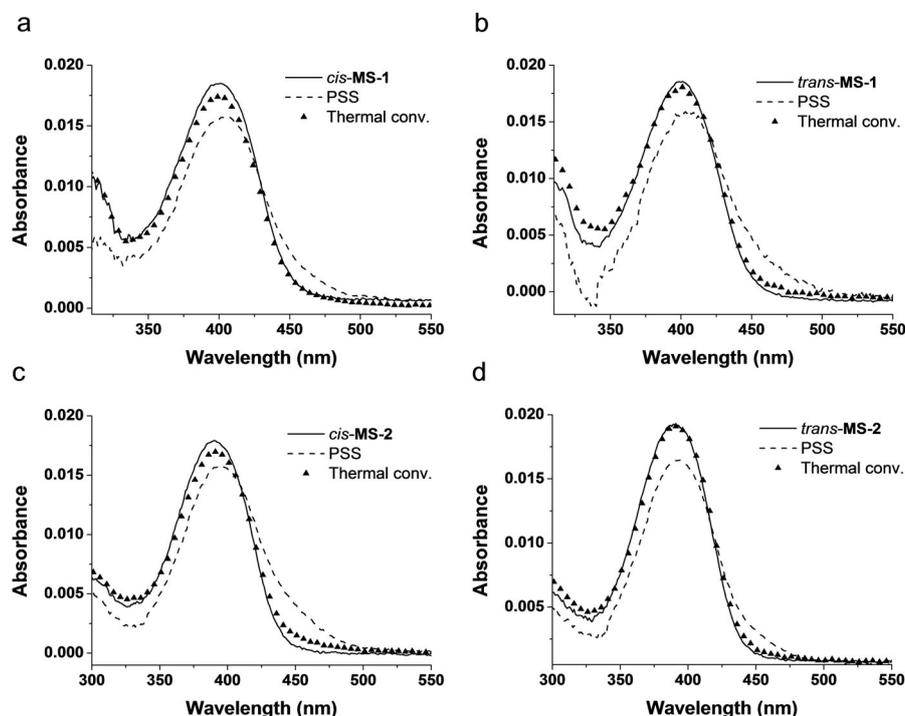Contact-angle measurements were performed on quartz sur-

Figure 2. UV/Vis spectra of surface-bound molecular motors *cis* and *trans* **MS-1** and **MS-2**. UV/Vis spectra of a) stable-*cis-***MS-1**, b) stable-*trans-***MS-1**, c) stable-*cis-***MS-2**, and d) stable-*trans-***MS-2** (solid lines) on quartz. Both isomers of the motors undergo photochemical isomerization upon irradiation at $\lambda_{max} = 365$ nm at $-5°C$ (dashed lines) and thermal isomerization upon standing at RT overnight (12 h) (▲).
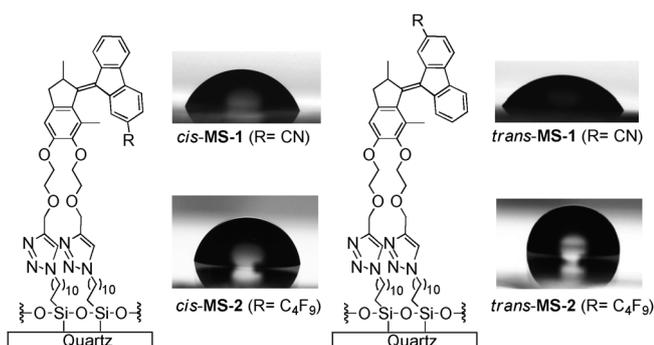
Figure 3. Pictures of water droplets on quartz surfaces modified by functionalized altitudinal molecular motors **16** and **17**.

contact angle in the case of *cis*-**MS-2** 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 **MS-1** and **MS-2** than the motors in solution, as indicated by the smaller redshift of the long-wavelength absorption band in their UV/Vis spectra (Schemes 4 and 5 versus Figure 2). 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[29].

Conclusion

From the above experimental observations it can be concluded that molecular motors that contain perfluorobutyl and cyano substituents were successfully synthesized and attached in an altitudinal orientation to quartz surfaces by using an interfacial 1,3-dipolar cycloaddition reaction. Furthermore, it was evident by UV/Vis 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 **16** and **17** provided different water contact angles depending on the polarity and orientation of the substituents. Research towards improved switching efficiency of the surface-bound motors and exploiting the surface wettability change is in progress.

Experimental Section

Detailed procedures for the synthesis of alkenes **16** and **17**; ^{1}H and ^{13}C NMR spectra for all compounds; Eyring plots of the kinetic studies of alkenes **16** and **17**; the procedure for preparing **SAM-1**, **MS-1**, and **MS-2**; and the pictures of water droplets on **MS-1** and **MS-2** can be found in the Supporting Information.

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