

# Adhesion of Photon-Driven Molecular Motors to Surfaces *via* 1,3-Dipolar Cycloadditions: Effect of Interfacial Interactions on Molecular Motion

Gregory T. Carroll,<sup>†</sup> Gábor London,<sup>†</sup> Tatiana Fernández Landaluze,<sup>†,‡</sup> Petra Rudolf,<sup>‡</sup> and Ben L. Feringa<sup>\*,†,‡</sup>

<sup>†</sup>Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands, and <sup>‡</sup>Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

**ABSTRACT** We report the attachment of altitudinal light-driven molecular motors to surfaces using 1,3-dipolar cycloaddition reactions. Molecular motors were designed containing azide or alkyne groups for attachment to alkyne- or azide-modified surfaces. Surface attachment was characterized by UV–vis, IR, XPS, and ellipsometry measurements. Surface-bound motors were found to undergo photochemical and thermal isomerizations consistent with unidirectional rotation in solution. Confinement at a surface was found to reduce the rate of the thermal isomerization process. The rate of thermal isomerization was also dependent on the surface coverage of the motors. In solution, changes in the UV–vis signal that accompany thermal isomerization can be fit with a single monoexponential decay. In contrast, thermal isomerization of the surface-bound motors does not follow a single monoexponential decay and was found to fit a biexponential decay. Both one- and two-legged motors were attached to surfaces. The kinetics of thermal isomerization was not affected by the valency of attachment, indicating that the changes in kinetics from solution to surface systems are related to interactions between the surface-bound motors.

**KEYWORDS:** molecular motors · surfaces · photochemistry · click chemistry · adhesion

The use of organic chemistry to create molecular and supramolecular systems that undergo switching processes has inspired the design of numerous systems that can be cycled between states through the application of various stimuli.<sup>1–10</sup> A key theme has been the construction of chemical systems that mimic dynamic functions of macroscopic machines with the ultimate goal of creating molecules that can perform useful work.<sup>11</sup> The utility of rotary motions in macroscopic and biological machines provides a strong motivation for studying nanoscale constructs containing molecular components that can undergo rotary motions.<sup>12–14</sup> Such systems are interesting not only in terms of understanding fundamental aspects of motion at the molecular level but also because biological systems have shown that rotary motions can be used to perform important functions. Two key examples are the ATP

synthase<sup>15–18</sup> and the bacterial flagellum,<sup>19</sup> both of which use rotary motion for biological needs. These natural machines show that nanoscale rotary motors not only are interesting for academic purposes but also indicate their potential future role in powering artificial nanomachines.<sup>20</sup> The potential for developing new technologies that utilize rotary motion has provided a strong impetus for understanding the physics of these biological motors as well as developing synthetic rotors<sup>12–14,21–32</sup> whose chemical composition and physical properties can be tailored for a given device. In order to harness the collective motions of rotary motors to perform useful tasks, it is expected that surface-confined systems<sup>30,33–36</sup> will be the most relevant, as these provide the opportunity to gain more order compared to solution-phase systems and minimize Brownian motion.<sup>37</sup> In this report we study assemblies of altitudinal motors that can undergo controlled rotary motions (Figure 1).

We previously reported the synthesis and surface reactivity of the altitudinal light-driven molecular motor **M1**, shown in Figure 2.<sup>33</sup> When attached to a surface, the motor retains its ability to undergo photochemical and thermal isomerization processes, reflecting the net unidirectional rotary behavior found in solution. Covalent attachment of the alkyne moieties of **M1** to an interface likely forces the system to rotate in an altitudinal manner with the axis approximately parallel to the surface, affording opportunities in attempting to control the coordinates of adsorbates. Upon absorption of a photon, the central overcrowded alkene undergoes geometric

\*Address correspondence to b.l.feringa@rug.nl.

Received for review October 25, 2010 and accepted December 13, 2010.

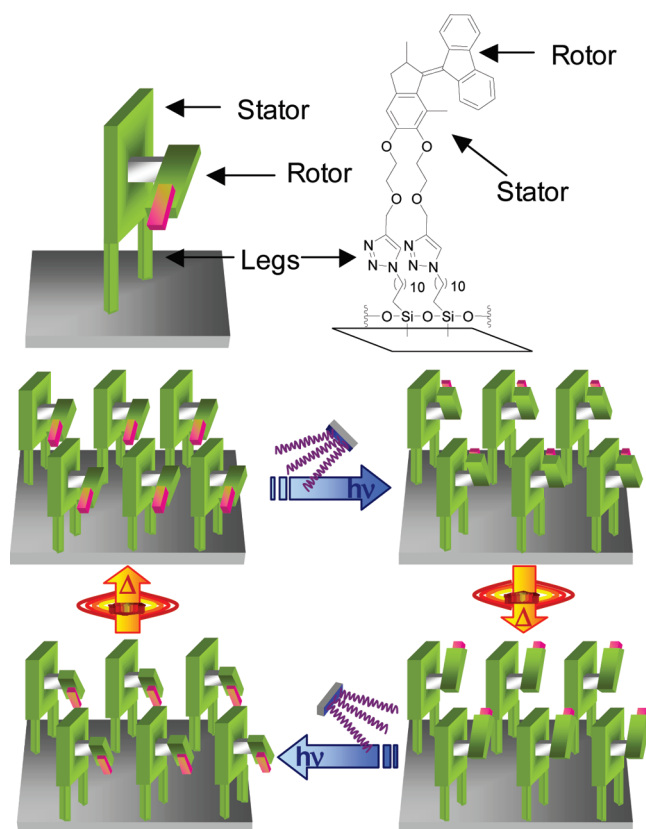
Published online January 5, 2011.  
10.1021/nn102876j

© 2011 American Chemical Society

isomerization (Figure 2). The ground-state product of the photochemical transformation is less stable than the original molecule due to a change in helicity and orientation of the stereocenter. The methyl substituent at the stereogenic center adopts the less stable pseudo-equatorial orientation instead of the more stable pseudo-axial orientation. In order to relieve strain, the motor undergoes an irreversible thermal helix inversion. During the thermal isomerization the methyl substituent at the stereogenic center changes from a pseudo-equatorial to a pseudo-axial orientation. A second photochemical and thermal isomerization completes the rotary cycle. Although much work has been done on these systems in regard to controlling the speed of rotation in solution,<sup>38</sup> macroscopic surface-attached systems<sup>33,34,39</sup> are largely considered to be more practical in converting rotary motion into mechanical work. The current paradigm regarding the thermal isomerization takes into account only the internal structure of the motor; yet key applications of these molecules are expected to involve interactions beyond steric hindrance within a single molecule. In this report we investigate the importance of confinement on the speed of rotation. We show that intermolecular interactions significantly affect the rate of thermal isomerization, a key step in the rotary cycle that ensures unidirectional rotation. The results are particularly significant with respect to key challenges in the area of prototypical nanomachinery: many molecular motors working in concert and the use of rotary molecular motors to induce the mechanical motion of an adsorbate. Additionally, the results indicate that a rotor of the kind described herein can undergo rotary motion in a confined environment in which intermolecular interactions impede thermal isomerization. Although our motivations are related to the construction of nanoscale machinery that is powered by controlled molecular motions, the system described herein has general implications for surface interactions and their effects on molecular mechanics.

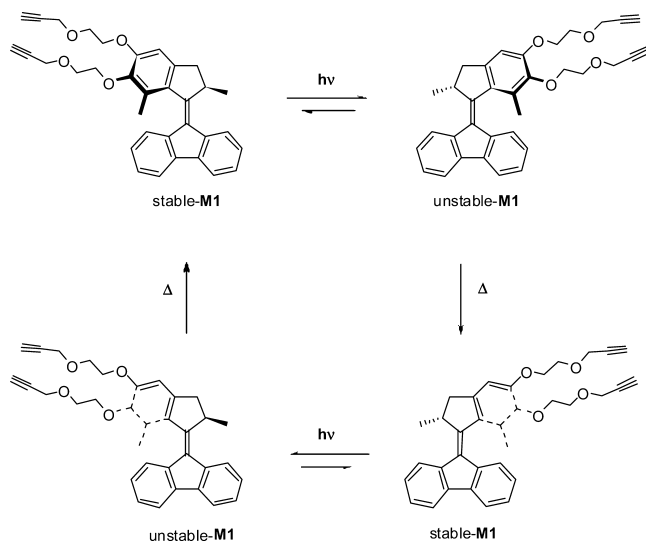
## RESULTS AND DISCUSSION

As described previously, silanated surfaces (**SAM 1**) containing azides were prepared on quartz and silicon substrates (Figure 3).<sup>33</sup> Immersion of substrates containing Si–OH surfaces in dilute solutions of silyl ethers is known to form stable coatings typically described as self-assembled monolayers (SAMs).<sup>40,41</sup> We found that immersion of piranha-cleaned quartz or Si/SiO<sub>2</sub> substrates in 1 mM solutions of compound **1** consistently gave organic coatings of 1.8 nm or less as measured by ellipsometry. The theoretical length of compound **1** is approximately 1.9 nm, consistent with a monolayer of the azide. A given substrate showed a thickness spread of no more than 0.1 nm when multiple areas of the substrate were measured, indicating a uniform coating. The coatings were stable to sonication in toluene and methanol. The most efficient procedure for achieving a



**Figure 1.** Controlled chemical attachment of light-driven altitudinal molecular motors to a solid substrate provides a monolayer of nanoscale motors. The four stages of the 360° rotary cycle can be addressed with light and heat.

high coverage of azide involved self-assembly from a 20:1 cyclohexane/THF solution containing a small quantity of H<sub>2</sub>O and HCl (see Supporting Information). Self-assembly in toluene reduced the coverage by approximately 50%. Self-assembly in cyclohexane without water or acid required two days to reach a film thickness of approximately 1.7 ± 0.1 nm. In addition to the



**Figure 2.** The rotary cycle of motor **M1** employed in surface attachment consists of four steps. A full cycle is achieved by a combination of light-driven and thermal helix inversion steps.



resulting UV signal was observed. Likewise, performing the surface reaction at 65 °C showed no difference in the intensity of the signal. Changing the immersion time provided a simple method to control the coverage. After removing the substrate at various times followed by sonication (2 min  $3\times$  in toluene and MeOH), the UV signal increased with reaction time, as expected for a covalent attachment to the interface (S1). The intensity of the UV signal and reaction time to reach saturation were dependent on the quality of the azide layer. A higher coverage of azide produced a higher UV signal and a longer reaction time to reach saturation. The higher density of motor was also evident in a higher ellipsometric thickness. The highest ellipsometric thickness of the motor layer obtained for the highest yield of azide is approximately 1.5 nm, which is close to the calculated length of 1.55 nm if the “legs” of **M1** are oriented normal to the substrate. The UV–vis and ellipsometry measurements previously reported<sup>33</sup> clearly indicate the presence of the motor on the azide-coated surfaces, which appears to be a single layer. Covalent attachment of the motor to the surface seems the likely adhesion mechanism given the control experiments described above. XPS measurements showed the disappearance of the azide signal and the presence of the triazole group, strongly supporting attachment through a 1,3-dipolar cycloaddition. To further support our claim, ATR-IR spectroscopy was performed on the surface (Figure 4). As noted above, the azide signal is clearly present on the silicon substrate. After reaction with the motor, the signal attenuates to the level of noise, providing further evidence for covalent modification of the azide layer. A reduction in the H<sub>2</sub>O contact angle from  $82 \pm 1^\circ$  to  $65 \pm 1^\circ$ , probably due to the ethylene glycol legs and triazole moiety of the surface linkage, was also previously used to characterize the coupling reaction and implies that the layer of motors is not so well packed as to screen the molecular components beneath the chromophore from a water droplet. Note that the H<sub>2</sub>O contact angle of a poly(styrene) film is approximately  $90^\circ$ .<sup>42</sup> Although not a perfect comparison, it provides a comparative value for a smooth film composed of aromatic units and aliphatic CH groups, both of which comprise the motor component of **M1**. The combination of characterization techniques and resistance to repeated cycles of sonication and washing strongly indicates that the motors are covalently bound to the interface.

An alternative approach one may opt for is to directly assemble a silanated version of the motor, **M2** (Figure S2). Although such an approach appears more efficient on paper, an advantage of the interfacial 1,3-dipolar cycloaddition of the motor rather than hydrolysis of a silanated motor is that multilayer formation during assembly or polymerization during storage or handling is no longer a possible undesirable outcome. Additionally, performing the reaction on the surface al-

lows one to bypass a step of the synthesis and the accompanying purification methods. In any case, we felt that it would be instructive to work with a silanated version of the motor. Our first attempt at forming the triazole in solution and assembling the silane **M2** resulted in a multilayer of  $77 \pm 8$  nm and an H<sub>2</sub>O contact angle of  $79 \pm 3^\circ$  on silicon. Polymerization of the silane was evident in the formation of a yellow particulate within ten minutes of mixing a THF solution containing silane and a small amount of H<sub>2</sub>O and acid in cyclohexane. Scanning electron microscopy (SEM) images show what appear to be fused particle-like aggregates (Figure S2). A stable coating was formed on silicon and quartz that was resistant to sonication. Irradiation of the film with UV light produced a yellow film that faded with time as the motor underwent thermal isomerization to the stable form. The changes in the UV–vis spectrum correspond to the changes found in solution and for the monolayer (Figure S2). Thinner films containing a thickness that corresponds to monolayer coverage could be obtained by reducing the concentration. For example, a film with an ellipsometric thickness of  $1.9 \pm 0.1$  nm could be obtained by assembling from a 0.01 mM solution (S3). Interestingly, self-assembly from THF showed very little coverage (0.3 nm ellipsometric thickness) and may be a result of competition with THF coordinating to the surface, as has been implicated when self-assembly is attempted on mica<sup>43</sup> (S3), although this comparison is imperfect, as mica is chemically different and may have a different mechanism of adhesion prevention. Although the system can be somewhat intractable, it provided an additional variant to study the kinetics of isomerization, as will be discussed below.

In order to more directly probe the feasibility of two-legged attachment as well as expand and test the versatility of the interfacial reaction, we synthesized motor **M3**, which contains two azides for attachment to an alkyne-modified surface, **SAM 2** (Figure 5). We silanated quartz and silicon wafers with *o*-(propargyloxy)-*N*-(triethoxysilylpropyl)urethane. After reaction of the film with **M3** under the same conditions for attaching **M1** to an azide surface, the UV–vis spectrum showed the presence of the motor on the surface only when catalyst was added to the reaction mixture (Figure S4). In the absence of catalyst or an alkyne film no motor was detected on the quartz surface. The distinctive IR and XPS signals corresponding to an azide functionality were used to probe the propensity for two-legged attachment.<sup>33,44</sup> Both the IR and XPS spectra show no evidence for unreacted azide in strong support that both legs of the motor react under the conditions employed (Figure 6).

As previously shown, **M1** can undergo photochemical isomerization followed by an irreversible thermal isomerization while confined at an interface.<sup>33</sup> The thermal isomerization is the rate-limiting step of the rotary cycle. Understanding how the structure of the motor af-

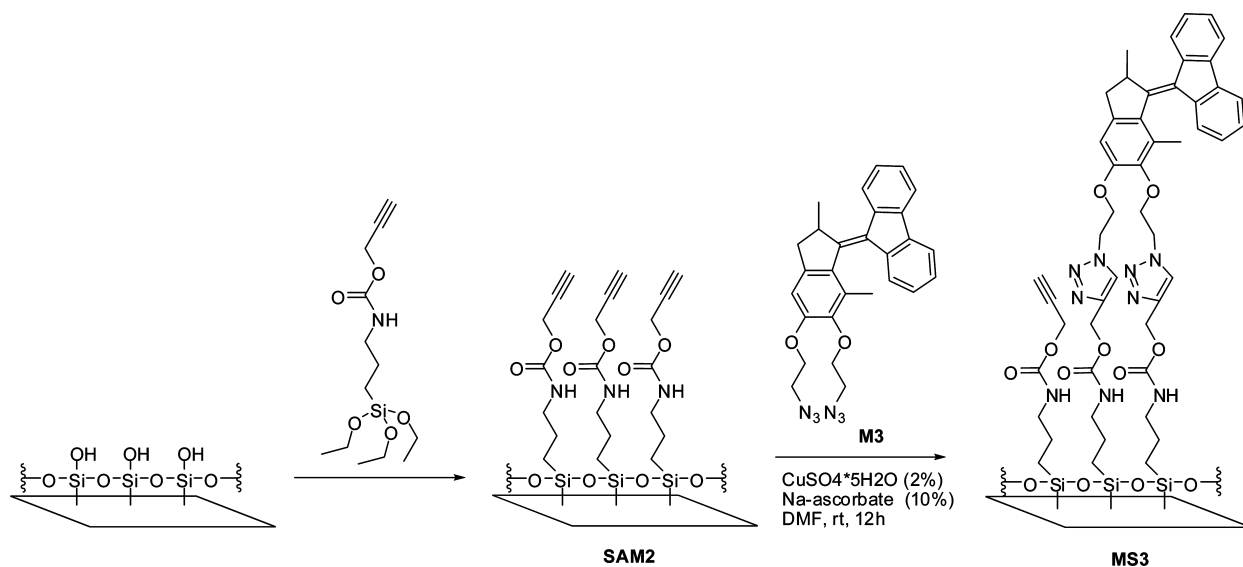


Figure 5. Attachment of an azide-containing motor (**M3**) to an alkyne-modified surface (**SAM 2**) to form **MS3**.

ffects the half-life of the thermal step has been key in increasing the speed of the motor. A general paradigm regarding the effect of substituents and ring size has been developed in order to design faster motors.<sup>38</sup> Although much progress has been made in synthesizing motors of various speeds, confinement and intermolecular effects on the speed of rotation have previously received little attention. In solution the thermal isomer-

ization of **M1** was found to proceed through a unimolecular process and a half-life of 90 s in methanol. In order to compare the surface-bound system with the solution analogue, we followed the time dependence of the changes in the UV spectrum during thermal isomerization at the interface using a surface that had a coverage of approximately 50% (Figure 7). In contrast to the solution experiments, fitting the thermal decay

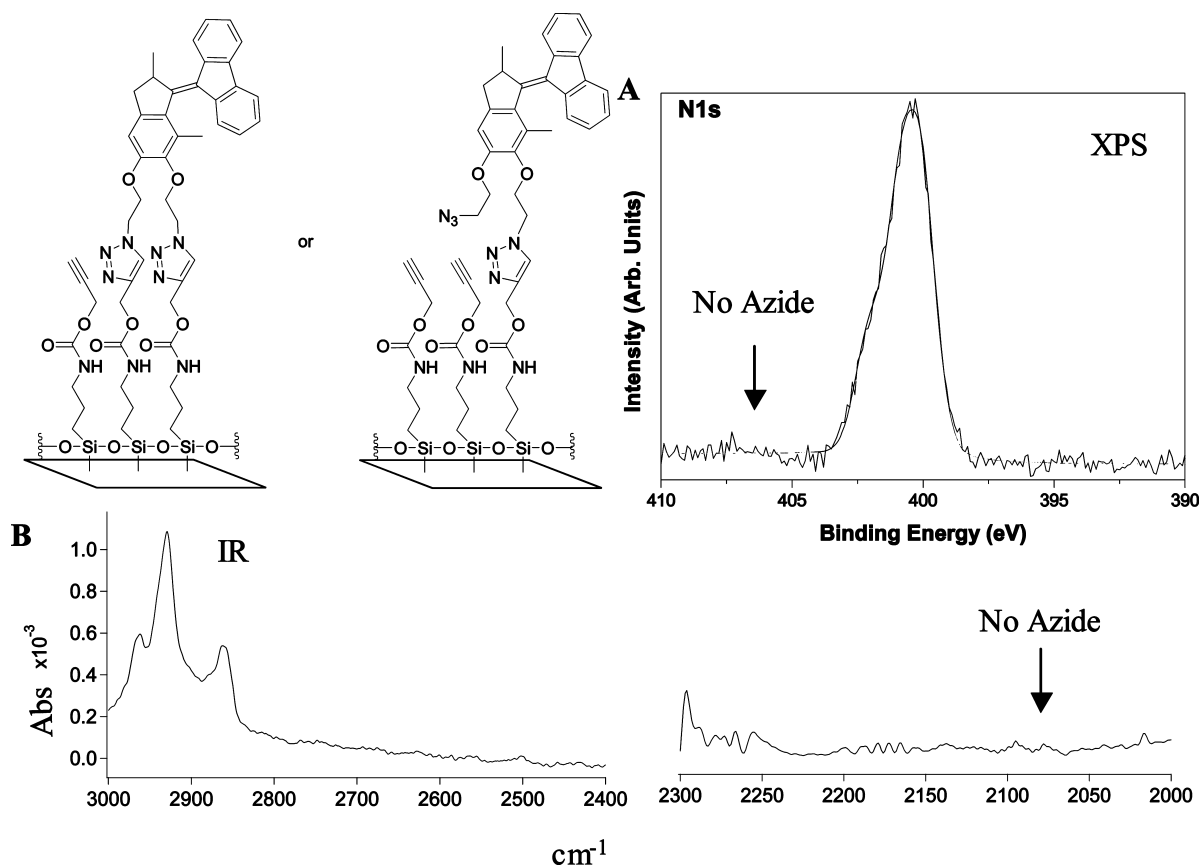
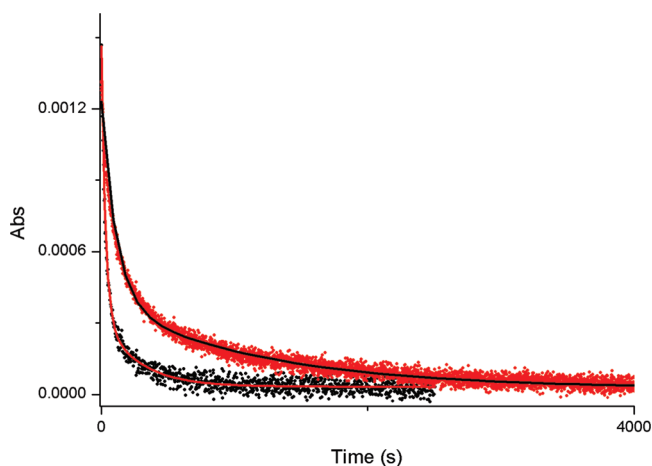


Figure 6. XPS (A) and ATR-IR (B) spectra of **MS3**. The absence of the signal corresponding to the azide in both spectra indicates that the motors attach to the surface through two legs. Azides show quite discernible signals with both techniques.<sup>33,44</sup>



of the signal at 439 nm suggested at least two processes occurring during the thermal isomerization that have half-lives that differ by an order of magnitude at 25 °C. The first half-life had a value of approximately 110 s, not so different from the half-life of 90 s measured in MeOH solution. More striking is the extraction of a second half-life of 1200 s, making the rotary cycle of the surface-bound ensemble considerably slower than in solution. We postulate the existence of at least two different processes, as evidenced by the biexponential decay of the UV signal corresponding to the unstable form of the motor. The biexponential fit may reflect environmental or configurational heterogeneities (i.e., surface roughness, defect sites, etc.) or multiple processes occurring during thermal isomerization when **M1** is clustered and bound to a substrate. As expected, higher temperatures increase the rate of thermal isomerization on the surface. For example, measurements performed at 40 °C gave a thermal decay for which half-lives of 30 and 270 s were obtained.

Interestingly, structurally different surface-confined systems have similarly shown a non-monoexponential decay corresponding to the kinetics of molecular conformational changes. For example, methylthiolate chemisorbed on a Ag(111) surface showed a biexponential decay for the lifetime of the first excited level of the symmetric C–H stretching mode.<sup>45</sup> Similarly, thin polymer films containing azobenzenes attached to side-chains have shown thermal rates that deviate from simple monoexponential behavior.<sup>46</sup> Regardless of the fitting procedure, it is clear that the thermal conformational change requires more time on the surface compared to solution. On the basis of our model of a layer of oriented motors covalently attached to a solid substrate, supramolecular interactions within a cluster of surface-bound motors seems to be the most plausible reason for the observed kinetics. The hypothesis was tested by constructing surfaces with a different coverage of motors and comparing the half-life for thermal isomerization. A potential advantage of the surface modification strategy presented herein is that better control over the density of the bound species can be obtained compared to direct self-assembly of a silane, which can assemble into dense clusters prior to surface attachment. Although the exact mechanism of interfacial 1,3-dipolar cycloadditions for small molecules is not known, we assume that for **M1** self-assembly into clusters at the surface does not precede covalent bond formation. For our arguments below we will assume random growth of the film without preaggregation or self-assembly; however we cannot explicitly rule out the latter. In order to understand the effect of surface coverage on the kinetics of the thermal isomerization, we examined four different coverages. We designate our highest covered surface as a saturation of 1.0. Using the UV–vis absorption signal at 379 nm as a guide, we studied surfaces that had a coverage that was approxi-



**Figure 7.** Thermal decay of UV signal of **MS1** (50% surface coverage) at 439 nm at 25 and 40 °C. Both data sets were fit with a biexponential decay, and hence two half-lives for the rate of thermal isomerization were calculated for each temperature. The half-lives at 25 °C are 110 and 1200 s. The half-lives at 40 °C are 30 and 270 s.

mately 50% and 25% the saturation coverage (saturation factor of 0.5 and 0.25, respectively). Additionally, we made use of our multilayer formed by assembly of the silane **M2** in order to probe a more extreme situation in which a given motor is more susceptible to axial interactions compared to a monolayer in which axial interactions could occur only when deviations from our model in Figure 1 occur (i.e., surface roughness, defects that considerably tilt the axle, adventitious impurities). The half-lives for the thermal isomerization are presented in Figure 8 (see Figure S5 for thermal decay curves). Both the fast and slower processes show a decrease in half-life with a decrease in the surface coverage. At full coverage, the half-lives are 280 and 4100 s, approximately twice that found for surfaces with 50% coverage. The most drastic change occurs on going from the monomolecular layer to the multilayer prepared by polymerization of the silane. The overlayer experienced by the motors in the multilayer film has a significant effect on the motors, which not only provides support for the idea that supramolecular interactions affect the speed of the rotary cycle but also indicates that the systems fabricated by the controlled dipolar cycloaddition do contain a reasonable degree of order as expected from chemoselective covalent bond formation of a small molecule with a surface.

One may consider that the two processes indicated by the biexponential fit reflect surface populations that are attached through one and two legs. If this was the case, then attaching a one-legged motor would show a monoexponential decay. In pursuit of understanding the valency of surface attachment on the kinetic behavior of the rotary cycle, a one-legged derivative of **M1**, **M4**, was synthesized (Figure 9). The UV–vis absorption spectrum is similar to that obtained for **M1** (Figure S6). The maximum of the longest wavelength absorption is blue-shifted by 3 nm in MeOH and 4 nm on the surface.



**Acknowledgment.** Financial support from NanoNed (G.L., G.T.C., T.F.L.), The Netherlands Organization for Scientific Research (NWO) (G.T.C., B.L.F.), Zernike Institute of Advanced Materials, the Materials Science Centre (MSC<sup>+</sup>), and the Foundation for Fundamental Research on Matter (FOM) (T.F.L., P.R.) is acknowledged.

**Supporting Information Available:** Additional experimental data on the synthesis and further characterization of alkenes **M2**, **M3**, and **M4** are provided in detail. Preparation and further spectroscopic characterization of surfaces is discussed. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. Artificial Molecular Machines. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391.
- Feringa, B. L., Ed. *Molecular Switches*; Wiley-VCH: Weinheim, 2001.
- Feringa, B. L. The Art of Building Small: From Molecular Switches to Molecular Motors. *J. Org. Chem.* **2007**, *72*, 6635–6652.
- Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. A Molecular Elevator. *Science* **2004**, *303*, 1845–1849.
- Duerr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*, revised ed.; Elsevier: Amsterdam, 2003.
- Mammana, A.; D'Urso, A.; Lauceri, R.; Purrello, R. Switching Off and On the Supramolecular Chiral Memory in Porphyrin Assemblies. *J. Am. Chem. Soc.* **2007**, *129*, 8062–8063.
- Randazzo, R.; Mammana, A.; D'Urso, A.; Lauceri, R.; Purrello, R. Reversible “Chiral Memory” in Ruthenium Tris(phenanthroline)-Anionic Porphyrin Complexes. *Angew. Chem., Int. Ed.* **2008**, *47*, 9879–9882.
- Jiang, S. G.; Liu, M. H. A Chiral Switch Based on Dye-Intercalated Layer-by-layer Assembled DNA Film. *Chem. Mater.* **2004**, *16*, 3985–3987.
- Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurple, G. W. Photoinduction of Fast, Reversible Translational Motion in a Hydrogen-Bonded Molecular Shuttle. *Science* **2001**, *291*, 2124–8.
- Kay, E. R.; Leigh, D. A.; Zerbetto, F. Synthetic Molecular Motors and Mechanical Machines. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.
- Browne, W. R.; Feringa, B. L. Making Molecular Machines Work. *Nat. Nanotechnol.* **2006**, *1*, 25–35.
- Koumura, N.; Zijlstra, R. W.; van Delden, R. A.; Harada, N.; Feringa, B. L. Light-Driven Unidirectional Molecular Rotor. *Nature* **1999**, *401*, 152–5.
- Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. A Reversible, Unidirectional Molecular Rotary Motor Driven by Chemical Energy. *Science* **2005**, *310*, 80–82.
- Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. Unidirectional Rotation in a Mechanically Interlocked Molecular Rotor. *Nature* **2003**, *424*, 174–179.
- Boyer, P. D. The ATP Synthase—A Splendid Molecular Machine. *Annu. Rev. Biochem.* **1997**, *66*, 717–749.
- Noji, H.; Yasuda, R.; Yoshida, M.; Kinosita, K. Direct Observation of the Rotation of F-1-ATPase. *Nature* **1997**, *386*, 299–302.
- Abrahams, J. P.; Leslie, A. G. W.; Lutter, R.; Walker, J. E. Structure at 2.8-Angstrom Resolution of F1-ATPase from Bovine Heart-Mitochondria. *Nature* **1994**, *370*, 621–628.
- Stock, D.; Leslie, A. G. W.; Walker, J. E. Molecular Architecture of the Rotary Motor in ATP Synthase. *Science* **1999**, *286*, 1700–1705.
- Macnab, R. M. How Bacteria Assemble Flagella. *Annu. Rev. Microbiol.* **2003**, *57*, 77–100.
- Morin, J. F.; Shirai, Y.; Tour, J. M. En Route to a Motorized Nanocar. *Org. Lett.* **2006**, *8*, 1713–1716.
- Gould, S. L.; Tranchemontagne, D.; Yaghi, O. M.; Garcia-Garibay, M. A. Amphidynamic Character of Crystalline MOF-5: Rotational Dynamics of Terephthalate Phenylenes in a Free-Volume, Sterically Unhindered Environment. *J. Am. Chem. Soc.* **2008**, *130*, 3246–3247.
- Winston, E. B.; Lowell, P. J.; Vacek, J.; Chocholousova, J.; Michl, J.; Price, J. C. Dipolar Molecular Rotors in the Metal-Organic Framework Crystal IRMOF-2. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5188–5191.
- Haidekker, M. A.; Theodorakis, E. A. Molecular Rotors—Fluorescent Biosensors for Viscosity and Flow. *Org. Biomol. Chem.* **2007**, *5*, 1669–1678.
- de Jonge, J. J.; Ratner, M. A.; de Leeuw, S. W.; Simonis, R. O.; Molecular Dipole Chains, I. I. I. Energy Transfer. *J. Phys. Chem. B* **2004**, *108*, 2666–2675.
- Rozenbaum, V. M. Coulomb Interactions in Two-Dimensional Lattice Structures. *Phys. Rev. B* **1996**, *53*, 6240–6255.
- Horansky, R. D.; Clarke, L. I.; Winston, E. B.; Price, J. C. Dipolar Rotor-Rotor Interactions in a Difluorobenzene Molecular Rotor Crystal. *Phys. Rev. B* **2006**, *74*, 0543061–05430612.
- Horansky, R. D.; Clarke, L. I.; Price, J. C.; Khuong, T. A. V.; Jarowski, P. D.; Garcia-Garibay, M. A. Dielectric Response of a Dipolar Molecular Rotor Crystal. *Phys. Rev. B* **2005**, *72*, 0143021–0143025.
- Clarke, L. I.; Horinek, D.; Kottas, G. S.; Varaksa, N.; Magnera, T. F.; Hinderer, T. P.; Horansky, R. D.; Michl, J.; Price, J. C. The Dielectric Response of Chloromethylsilyl and Dichloromethylsilyl Dipolar Rotors on Fused Silica Surfaces. *Nanotechnology* **2002**, *13*, 533–540.
- Zheng, X. L.; Mulcahy, M. E.; Horinek, D.; Galeotti, F.; Magnera, T. F.; Michl, J. Dipolar and Nonpolar Altitudinal Molecular Rotors Mounted on an Au(111) Surface. *J. Am. Chem. Soc.* **2004**, *126*, 4540–4542.
- Baber, A. E.; Tierney, H. L.; Sykes, E. C. H. A Quantitative Single-Molecule Study of Thioether Molecular Rotors. *ACS Nano* **2008**, *2*, 2385–2391.
- Maksymovych, P.; Sorescu, D. C.; Dougherty, D.; Yates, J. T. Surface Bonding and Dynamical Behavior of the CH<sub>3</sub>SH Molecule on Au(111). *J. Phys. Chem. B* **2005**, *109*, 22463–22468.
- Gao, L.; Liu, Q.; Zhang, Y. Y.; Jiang, N.; Zhang, H. G.; Cheng, Z. H.; Qiu, W. F.; Du, S. X.; Liu, Y. Q.; Hofer, W. A.; Gao, H. J. Constructing an Array of Anchored Single-Molecule Rotors on Gold Surfaces. *Phys. Rev. Lett.* **2008**, *101*, 197209–197212.
- London, G.; Carroll, G. T.; Landaluce, T. F.; Pollard, M. M.; Rudolf, P.; Feringa, B. L. Light-Driven Altitudinal Molecular Motors on Surfaces. *Chem. Commun.* **2009**, 1712–1714.
- Michl, J.; Sykes, E. C. H. Molecular Rotors and Motors: Recent Advances and Future Challenges. *ACS Nano* **2009**, *3*, 1042–1048.
- Bellisario, D. O.; Baber, A. E.; Tierney, H. L.; Sykes, E. C. H. Engineering Dislocation Networks for the Directed Assembly of Two-Dimensional Rotor Arrays. *J. Phys. Chem. C* **2009**, *113*, 5895–5898.
- Balzani, V.; Credi, A.; Venturi, M. Molecular Machines Working on Surfaces and at Interfaces. *Chemphyschem* **2008**, *9*, 202–220.
- Berg, H. C. *Random Walks in Biology*; Princeton University Press: Princeton, 1993.
- Pollard, M. M.; Klok, M.; Pijper, D.; Feringa, B. L. Rate Acceleration of Light-Driven Rotary Molecular Motors. *Adv. Funct. Mater.* **2007**, *17*, 718–729.
- Carroll, G. T.; Pollard, M. M.; van Delden, R.; Feringa, B. L. Controlled Rotary Motion of Light-Driven Molecular Motors Assembled on a Gold Film. *Chem. Sci.* **2010**, *1*, 97–101.
- Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- Park, E. J.; Carroll, G. T.; Turro, N. J.; Koberstein, J. T. Shedding Light on Surfaces—Using Photons to Transform and Pattern Material Surfaces. *Soft Matter* **2009**, *5*, 36–50.
- Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
- Peanasky, J.; Schneider, H. M.; Granick, S.; Kessel, C. R. Self-Assembled Monolayers on Mica for Experiments Utilizing



- the Surface Forces Apparatus. *Langmuir* **1995**, *11*, 953–962.
44. Lummerstorfer, T.; Hoffmann, H. Click Chemistry on Surfaces: 1,3-Dipolar Cycloaddition Reactions of Azide-Terminated Monolayers on Silica. *J. Phys. Chem. B* **2004**, *108*, 3963–3966.
  45. Harris, A. L.; Rothberg, L.; Dubois, L. H.; Levinos, N. J.; Dhar, L. Molecular Vibrational-Energy Relaxation at a Metal-Surface—Methyl Thiolate on Ag(111). *Phys. Rev. Lett.* **1990**, *64*, 2086–2089.
  46. Barrett, C.; Natansohn, A.; Rochon, P. Thermal Cis-Trans Isomerization Rates of Azobenzenes Bound in the Side-Chain of Some Copolymers and Blends. *Macromolecules* **1994**, *27*, 4781–4786.
  47. Carroll, G. T.; Wang, D. N.; Turro, N. J.; Koberstein, J. T. Photons to Illuminate the Universe of Sugar Diversity through Bioarrays. *Glycoconj. J.* **2008**, *25*, 5–10.
  48. Carroll, G. T.; Wang, D.; Turro, N. J.; Koberstein, J. T. Photochemical Micropatterning of Carbohydrates on a Surface. *Langmuir* **2006**, *22*, 2899–2905.
  49. Wang, S.; Song, Y.; Jiang, L. Photoresponsive Surfaces with Controllable Wettability. *J. Photochem. Photobiol. C: Photochem. Rev.* **2007**, *8*, 18–29.
  50. Lim, H. S.; Han, J. T.; Kwak, D.; Jin, M.; Cho, K. Photoreversibly Switchable Superhydrophobic Surface with Erasable and Rewritable Pattern. *J. Am. Chem. Soc.* **2006**, *128*, 14458–14459.
  51. Oh, S. K.; Nakagawa, M.; Ichimura, K. Photocontrol of Liquid Motion on an Azobenzene Monolayer. *J. Mater. Chem.* **2002**, *12*, 2262–2269.