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## An ultrafast surface-bound photo-active molecular motor†

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Jérôme Vachon,<sup>a</sup> Gregory T. Carroll,<sup>a</sup> Michael M. Pollard,<sup>a</sup> Emile M. Mes,<sup>b</sup> Albert M. Brouwer<sup>b</sup> and Ben L. Feringa<sup>\*a</sup>

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We report the synthesis and surface attachment of an ultrafast light-driven rotary molecular motor. Transient absorption spectroscopy revealed that the half-life of the rate determining thermal step of the rotary cycle in solution is  $38 \pm 1$  ns, the shortest yet observed, making this the fastest molecular motor reported. Incorporation of acetylene legs into the structure allowed the motors to be grafted to azide-modified quartz and silicon substrates using the “click” 1,3-dipolar cycloaddition reaction.

### Introduction

Molecular motors are ubiquitous in nature where they are used for a variety of tasks including transport, cellular translocation, and ATP synthesis.<sup>1</sup> Biological motors are able to generate a considerable torque (up to  $4500 \text{ pN nm}^{-1}$ ) and can rotate large objects through solution. A surface-bound ATPase is a fine example as this molecular motor has been used to rotate a  $2.6 \mu\text{m}$  actin filament through a solution.<sup>2</sup> Reminiscent of the molecular machinery of nature, many nanoscale systems that undergo controlled and reversible structural changes have been reported.<sup>3</sup>

Molecular rotary motors based on overcrowded alkenes can undergo light-driven unidirectional rotation, providing considerable possibilities in powering future nanomachines (Fig. 1). It is anticipated that in order to harness work from an assembly of synthetic rotary molecular motors, the motors should be sufficiently fast in order to compete with Brownian motion and the motors should be attached to a surface through two “legs” which limit its positional and orientational degrees of freedom.<sup>4</sup> We recently described second generation molecular motors of type 1 bearing a 5-membered-ring upper-half and 6-membered ring (**1**, X = O or S) or 7-membered ring (**1**, X =  $\text{CH}_2\text{-CH}_2$ ) lower-half connected by a central carbon-carbon bond which acts as the axis of rotation (Fig. 1).<sup>5</sup> These compounds display repetitive unidirectional rotation when irradiated with UV light. Irradiation induces a photochemical *cis-trans* isomerization (on a picoseconds time scale),<sup>6</sup> and is

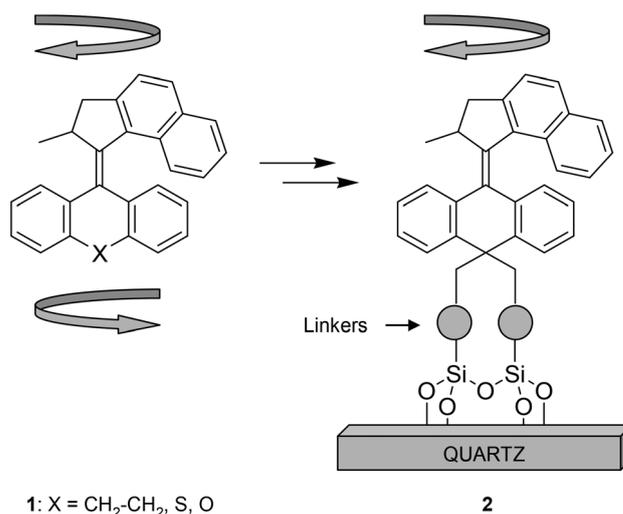


Fig. 1 Translation of unidirectional rotary motion in solution into absolute rotary motion is achieved by grafting the stator half of the motor to a quartz surface.

followed by a thermal helix inversion, which is the rate limiting step.<sup>7</sup> These motors can achieve rotary cycles at a MHz time scale at room temperature making them the fastest synthetic rotary motors described so far.

Anchoring ultrafast molecular motors to a solid substrate is of importance to develop macroscopic systems that can transmit their actions into work upon their surrounding environment.<sup>8</sup> In this paper we report the synthesis and characterization of an acetylene-functionalised ultra-fast motor and demonstrate that monolayers of the motor can be grafted to azide-modified quartz and silicon substrates. The speed of the rate-limiting thermal isomerisation step of the rotary cycle has been measured using transient absorption spectroscopy

<sup>a</sup>Department of Organic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: B.L.Feringa@rug.nl; Fax: +31 50 363 4235

<sup>b</sup>Van't Hoff Institute for Molecular Sciences, University of Amsterdam, P.O. Box 94157, 1090 GD Amsterdam, The Netherlands

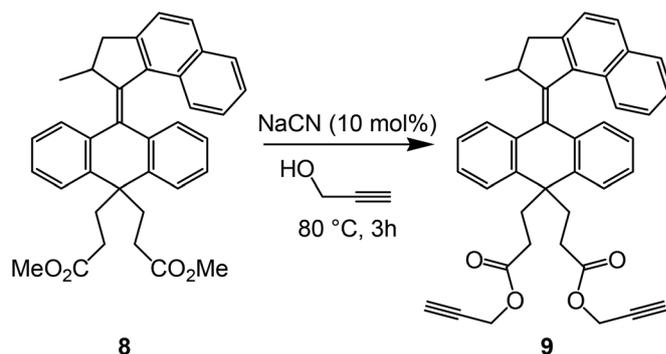
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3pp50208b

and shows that this new motor is 3 times faster than our previous fastest molecular motor (*i.e.* compound **1**, X = S).

## Results and discussion

In order to preserve the ultrafast properties of molecular motors of type **1**, we employed the same five-membered ring upper-half “rotor” previously used for several molecular motors having a low barrier to the rate-limiting thermal isomerization steps in the 4-step rotary cycle.<sup>5,9,10</sup> Two ester moieties were introduced in the lower-half “stator” of the molecule to facilitate its attachment to a surface. Two “legs” are essential to ensure that the top-half rotates unidirectionally relative to the surface when illuminated. When only one leg is attached, the system can spin randomly about a C–C single bond. The preparation of the new motor molecule begins with the condensation in refluxing methanol of hydrazine onto a previously described thioketone **3** (Scheme 1).<sup>11</sup> The hydrazone **4** was formed in 67% yield and was further oxidized using MnO<sub>2</sub> to generate the diazo-compound **5** which was used in the subsequent step without purification. Treatment of **5** with freshly prepared thioketone **6**<sup>10</sup> led to a Barton–Kellogg coupling reaction generating episulfide **7** in 53% yield.<sup>12</sup> Desulfurization of **7** was achieved in refluxing *p*-xylene in the presence of PPh<sub>3</sub> which generated overcrowded alkene **8** in 94% yield.

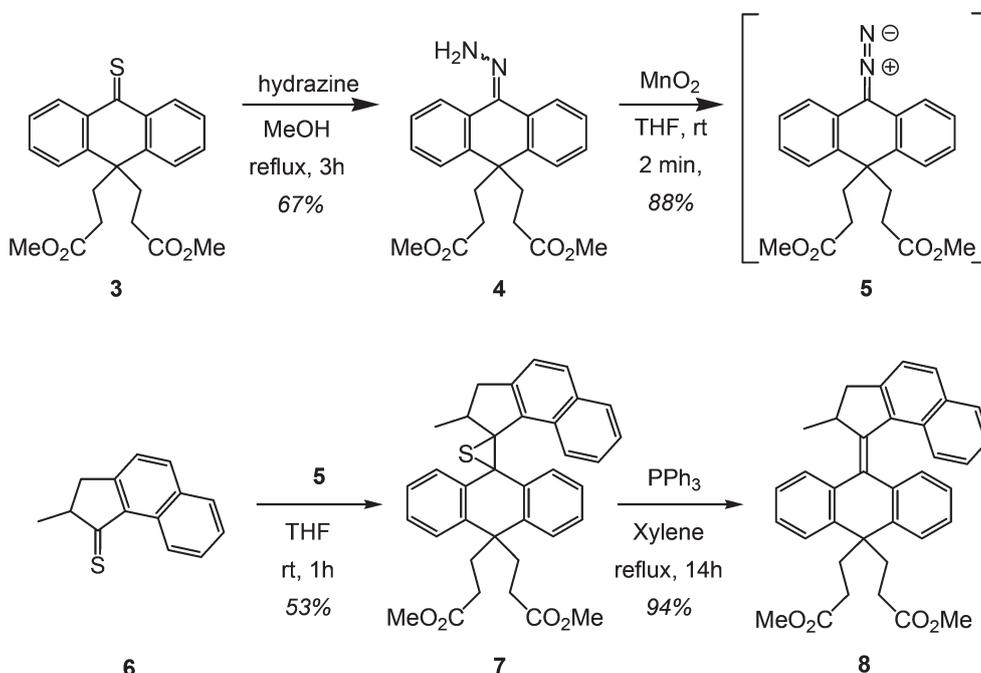
The two methyl ester legs of compound **7** provide very versatile functionalities, allowing a wide range of transformations *via* transesterification reactions with various alcohols. Transesterification with propargylic alcohol in the presence of sodium cyanide as a catalyst afforded compound **9** in 70% yield (Scheme 2), which bears two terminal acetylene groups.



**Scheme 2** Sodium cyanide-catalysed transesterification of compound **8** with propargylic alcohol.

While the use of a cyanide catalyst is particularly well known for transamidation reactions,<sup>13</sup> for instance in peptide chemistry, its use for transesterification reactions is scarce and historically used to exchange methyl esters to ethyl esters.<sup>14</sup> The acetylene legs provide a highly versatile group for attaching the motors to azide-functionalized materials and in our case macroscopic solid substrates modified with azides.<sup>15</sup> Such surfaces are easily accessible and air and moisture inert.

Prior to surface attachment, we studied the rotational behavior of molecule **9** in solution. Since the structure was similar to ultra-fast molecular motor **1**, we anticipated that it would also have a low barrier for the thermal isomerisation of the unstable isomer. As for compound **1**, UV-vis experiments were first attempted with the use of a low melting point solvent in order to “freeze” the unstable isomer generated after irradiation before it undergoes thermal isomerization to its



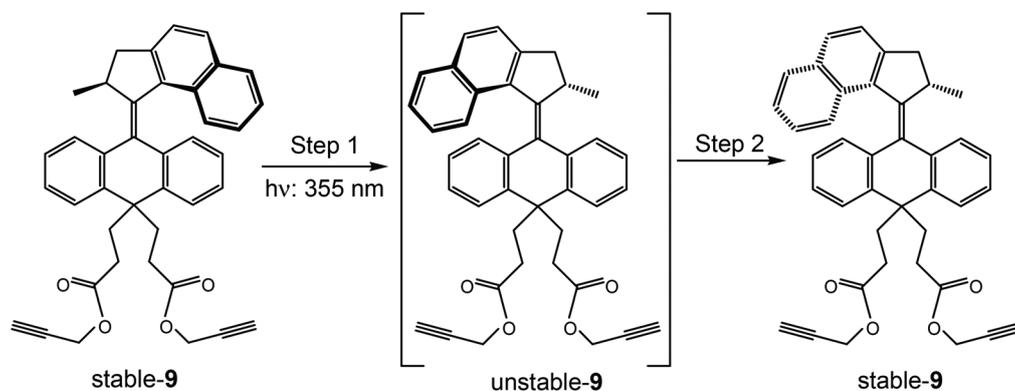
**Scheme 1** Synthesis of molecular motor **8** *via* a Barton–Kellogg reaction between **5** and **6**.

stable isomer. Isopentane (mp = 113 K) or propane (mp = 85.5 K) are usually appropriate solvents for this kind of experiment, but unfortunately **9** was found to be insoluble in these solvents. The use of a drop of CH<sub>2</sub>Cl<sub>2</sub> to ensure that **9** dissolved completely was unsuitable as the solvent mixture melted at around 90 K. Similarly to compound **1**, this fast thermal isomerisation step has thus been studied by an alternative approach, namely ns-pulsed laser transient absorption (TA) spectroscopy.<sup>5</sup> This technique, which is particularly well-suited to study ultra-fast conformational changes (on timescales of picoseconds), is the method of choice to probe photo-excited state dynamics.<sup>16</sup>

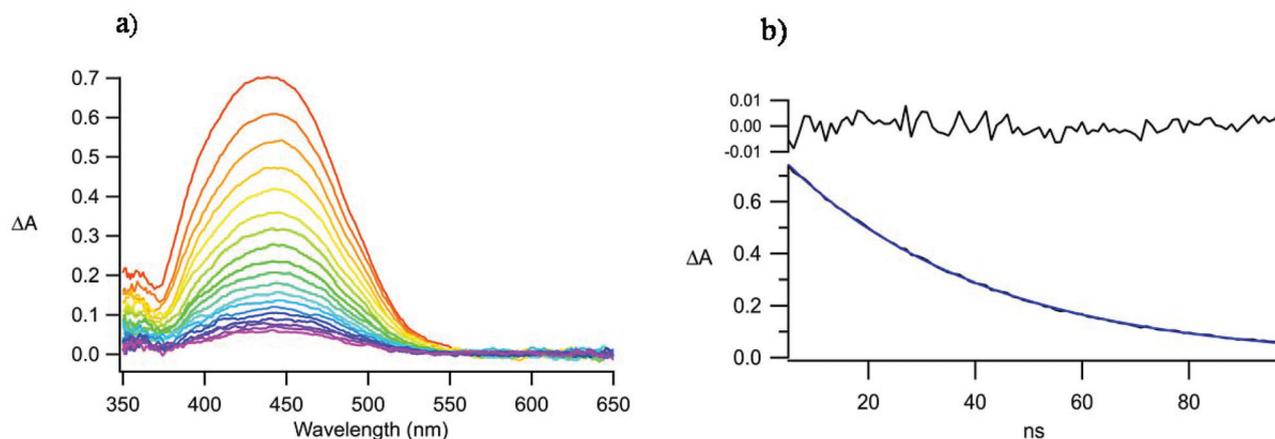
Experiments were performed in *n*-hexane where compound **9** possesses a local absorption maximum at 355 nm ( $A_{355} = 1.07$ ,  $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>). Irradiation of a solution of stable-**9** generates a new, red-shifted absorption centered at about 445 nm. Based on its similarity to the absorption spectra of related second generation motors of type **1**, the formation of this new absorption is consistent with the formation of unstable-**9** (Step 1, Scheme 3).<sup>5</sup> Using this technique, it is thus possible to determine the lifetime of unstable-**9**, which

thermally regenerates the stable isomer of compound **9** (Step 2, Scheme 3). Experimentally, the sample was excited at 5 Hz with a Nd:YAG laser (7 ns width, 3.6 mJ per pulse) and probed with a flash lamp at 10 Hz. The probe light was detected using an image intensified CCD camera at electronically controlled time delays. In this way, the transmission of the sample was measured before the laser pulse and a certain time after the laser pulse. The pump-probe delay time was incremented in 98 steps of 1 ns. At each delay 50 measurements were averaged to give the spectra shown in Fig. 2a. The laser light is filtered off by using a 375 nm filter in front of the detector. The lifetime of the unstable form of **9** was estimated to be approximately  $38 \pm 1$  ns (Fig. 2b) which makes it the fastest light-driven rotary molecular motor reported so far.<sup>5</sup> During these experiments, very little decomposition of the compound was observed proving that the  $\Delta A$  observed could not be attributed to photodegradation of the molecule, but rather the presence of the unstable isomer generated after photo-excitation (see ESI, Fig. S11†).

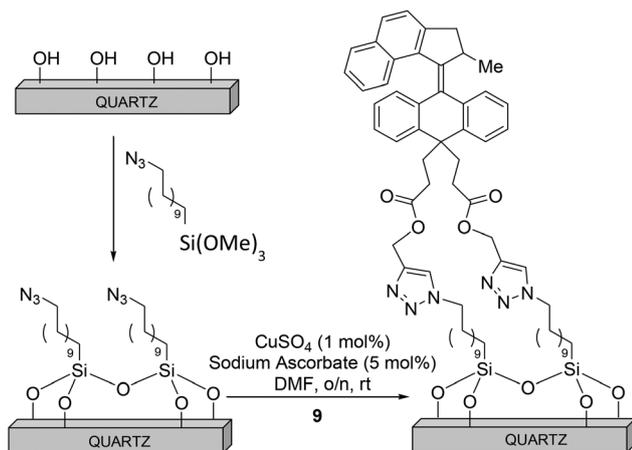
Harnessing the rotary cycle to perform work while the motor-molecule is in solution is exceptionally challenging due



**Scheme 3** Generation of unstable-**9** by photoirradiation of stable-**9** with UV-light ( $\lambda_{\text{max}} = 355 \text{ nm}$ , step 1), which thermally isomerizes to stable-**9** (step 2).



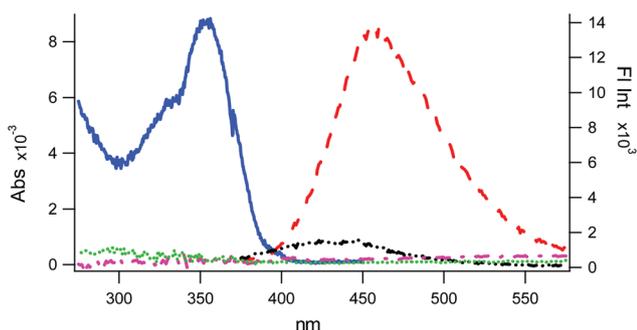
**Fig. 2** (a) Absorption difference spectra of **9** in *n*-hexane solution after a 355 nm 7 ns laser pulse (shown at 5 ns time increments) and (b) the decay of the transient absorption at 442 nm in time, fitted mono-exponentially. The fitted decay time was found to be  $38 \pm 1$  ns.



**Fig. 3** Preparation of an azide functionalized quartz surface for subsequent grafting of **9** via an interfacial copper catalysed 1,3-dipolar cycloaddition reaction.

to Brownian motion. One way to limit Brownian motion is to adhere the motor to a macroscopic solid surface.<sup>17,15,11b</sup> Azide-terminated self-assembled monolayers (SAMs) on quartz surfaces were prepared following a previously reported procedure (Fig. 3).<sup>15</sup> The surfaces were immersed in a solution of the azide in cyclohexane at room temperature for approximately 12 h. The slides were then sonicated in toluene ( $2 \times 2$  min) and methanol (2 min), and dried with an argon flux. Compound **9** was grafted to the resulting surfaces by immersion of the azide SAM in a 1 mM solution of **9** in the presence of a catalytic mixture of  $\text{CuSO}_4$  and sodium ascorbate in DMF, for approximately 12 h at room temperature. After removal from the solution, the surfaces were washed by sonicating in DMF, methanol and water (2 min each), and dried with an argon flux.

To ensure that the molecule is grafted on the surface, the UV-vis absorption spectra of **9** in *n*-hexane solution ( $c = 10^{-5}$  mol  $\text{L}^{-1}$ ) (ESI, Fig. S11†) and grafted to the surface of a quartz slide (Fig. 4) were compared. Both spectra display a similar



**Fig. 4** UV-vis spectra of **9** grafted onto an azide-modified quartz surface (blue, solid); quartz surface functionalized with azide, after immersion in solution containing **9** without copper catalyst (pink, dotted-dashed); and unmodified  $\text{SiO}_2/\text{Si}$  quartz surface after immersion in solution of **9** with copper catalyst (green, dotted). Emission spectra ( $\lambda_{\text{ex}} = 355$  nm) of **9** grafted onto an azide-modified quartz surface (red dotted) and unmodified quartz surface (black, dashed-dotted-dotted).

absorption profile, indicating that the desired molecule is attached to the surface. Neither immersion of the azide-functionalized quartz into a solution of **9** without catalyst nor immersion of an underivatized quartz slide into a solution of compound **9** with catalyst displayed any significant absorption in their UV-vis spectrum. Similarly, the fluorescence spectrum of the surface (Fig. 4) matches the solution spectrum (ESI, S10†). ATR-IR shows the disappearance of the band corresponding to the azide (ESI, S12†). The thickness of the organic layer after reaction with compound **9** increased by  $0.8 \pm 0.1$  nm as determined by ellipsometry, corresponding to a controlled adhesion of a single layer of motors. Further, the  $\text{H}_2\text{O}$  contact angle decreased from approximately  $78 \pm 1^\circ$  to  $65 \pm 2^\circ$  as found previously for a similar system.<sup>11</sup>

## Conclusions

In conclusion, we have synthesized a new molecular motor, **9**, which bears a five-membered ring upper-half and a six-membered ring lower-half with two terminal acetylene legs. Upon irradiation of **9** in hexane at 355 nm the motor undergoes photochemical isomerisation. Following photo-isomerisation, the molecular motor undergoes a very fast thermal isomerisation which has been monitored by transient absorption spectroscopy. The time constant of the thermal step is  $38 \pm 1$  nanoseconds, which corresponds to a  $360^\circ$  rotation rate of  $>12$  MHz under optimal conditions in solution. Using the “click” copper-catalysed Huisgen cycloaddition reaction, the motor-molecule can be easily grafted to quartz and  $\text{Si}/\text{SiO}_2$  surfaces that have been modified with azide functionalities. Current efforts are ongoing in the preparation of a similar molecular motor with functionalities incorporated into the upper-half rotor of the molecule, allowing for systems with a higher amplitude of rotation to be developed.

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