

# Recent progress on nanovehicles

Yasuhiro Shirai, Jean-François Morin, Takashi Sasaki, Jason M. Guerrero and James M. Tour\*

Received 4th August 2006

First published as an Advance Article on the web 23rd August 2006

DOI: 10.1039/b514700j

Nanovehicles are a new class of molecular machines consisting of a molecular scale chassis, axles, and wheels, that can roll across solid surfaces with structurally defined directions making them of interest to synthetic chemists, surface scientists, chemical engineers, and the general car enthusiast. In this *tutorial review*, following a brief introduction to the development of nanomachines, our recent progress on the nanovehicle project is presented including the design, synthesis, and testing of a series of nanocars, nanotrucks, and motorized nanocars.

## 1. Introduction

The quest for functional molecular devices has stimulated the design and synthesis of a variety of organic compounds such as motors,<sup>1–4</sup> rotors,<sup>5</sup> barrows,<sup>6</sup> scissors,<sup>7</sup> turnstiles,<sup>8</sup> elevators,<sup>9</sup> shuttles,<sup>10,11</sup> hinges,<sup>12</sup> switches,<sup>13</sup> and more<sup>14,15</sup> that resemble macroscopic machinery. This is in part inspired by the visionary ideas of Richard Feynman almost half a century ago.<sup>16</sup> It is also driven by the continued quest to miniaturize machinery in our current scientific and technological disciplines.

One of the most advanced current fabrication methods, the “top-down” approach to miniaturization in the semiconductor industry, is nearing its limits in scaling.<sup>17</sup> The strategy used in the top-down approach is to shrink, and shrink again, a macroscopic entity using photolithography and the related

techniques<sup>18,19</sup> to reach an equivalent microscopic entity. It is thought that the inherent limitations of this strategy



**Takashi Sasaki**

working on synthesis and imaging of fullerene/carborane molecular machines and motors.

Takashi Sasaki was born in 1980 in Yokohama, Japan and soon moved to the US in the late 80's. As an undergraduate at Carnegie Mellon University (CMU), he acquired research experiences under Professor Stuart Staley, Professor Bertil Eliasson of Umeå University, and Professor Tadashi Sugawara of University of Tokyo. After receiving his BS with Honors from CMU, he is currently pursuing his PhD under Professor James M. Tour

Rice University, Departments of Chemistry and Mechanical Engineering and Materials Science, and the Smalley Institute for Nanoscale Science & Technology, MS 222, 6100 Main St., Houston, TX 77005, USA.  
E-mail: tour@rice.edu; Fax: 713 348 6250; Tel: 713 348 6246



**Yasuhiro Shirai**

His graduate research focuses on the design and synthesis of fullerene-functionalized molecular devices and machines.

Yasuhiro Shirai received his BS degree in Electrical Engineering from the Kanagawa University (Japan), and worked for the Nippon Avionics Co., Ltd. in 1993–2000. He was also an exchange student at the University of Kansas in 1997–1998, and then he studied anion coordination chemistry under the supervision of Professor Kristin Bowman-James in 2000–2001. He joined Professor Tour's group in 2001, and he is currently working toward a PhD in Chemistry.

Jean-François Morin received his BSc in chemistry from the Université Laval, Quebec City, Canada, in 2000. Then, he received



**Jean-François Morin**

an NSERC scholarship to undertake a PhD with Professor Mario Leclerc at CERSIM, Université Laval where his work focused on the design, synthesis and characterization of oligo- and poly(2,7-carbazole)s for electroluminescent devices and field-effect transistors. After receiving his PhD in 2004, he joined Professor James M. Tour's group as a FQRNT and NSERC postdoctoral research associate where he worked on the development of self-propelled nanomachines on surfaces. In 2006 he moved back to Université Laval, Department of Chemistry, as an Assistant Professor. His current research activities include the synthesis and characterization of organic nanotubes, nanoscale machinery and rotaxane-based nanomaterials for photovoltaic applications.

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would lead to a dead end in the next few years. For instance, silicon's band structure disappears when silicon layers are just a few atoms thick.<sup>17</sup> Photolithography and other related techniques, also used for microelectromechanical systems (MEMS) fabrication, are limited by the wavelengths at which they operate.

On the other hand, nanocars synthesized in our laboratory are each calculated to be approximately  $3 \times 4$  nm in size, and can be produced on the  $\sim 30$  mg scale ( $\sim 3.2 \times 10^{18}$  nanocars) using small 100 ml laboratory reaction flasks, or more nanocars than the number of automobiles made in the history of the world (63 million automobiles were produced in 2005). It would take 30 nanocars, side by side, to span the 90 nm width of a small line in the most advanced logic chip being made today.<sup>17</sup> Miniaturization can be pushed further beyond the limit set by the current top-down approach if we could construct functional micro- or nanoscopic entities using individual molecules, designed from the "bottom-up." The bottom-up approach is quite natural in that all systems in nature are constructed bottom-up. However, we are far behind what nature has achieved in the biological process.<sup>20</sup> All biological nanomachines are quite complicated, and currently we cannot produce anything close to them. In 2000, the integration of a biological motor, ATPase, with nanoscale-engineered systems was published.<sup>21</sup> However, it is still difficult to construct a motor that is itself as complicated as ATPase, and it would be almost hopeless to try such a task given our current tools in synthetic organic chemistry. Consequently, molecular scientists have turned their attention to much simpler systems where it may be possible to construct and understand machinery at the molecular level, and afterwards progress toward more sophisticated and useful machinery based on this knowledge.

In this tutorial review, following a brief introduction to the development of nanomachines, recent progress in our laboratories toward the design, synthesis, and testing of nanovehicles including nanocars, nanotrucks, and motorized nanocars, is described.

## 2. Development of nanomachines

The vast majority of the molecular machines cited at the beginning of this review were designed and synthesized to operate in the solution phase because of the abundant solution phase analytical tools available to the chemist. However, for useful nanomachines with mechanical functions, they will eventually need to be integrated into devices that interface surrounding systems. For example, the biological nanomachine ATPase is anchored in a biological membrane in order to interface with its surroundings, the chemical gradient across the membrane. Viable approaches to this interface issue have yet to be demonstrated, however, this necessity adds extra levels and difficulties to nanomachine design.

Despite such difficulties, several examples of nanomachines whose operation can be proven in the solid state and/or on solid surfaces, not in the solution state, have been published. Following is a short summary of such nanomachines, which are designed to (1) operate in a crystalline solid, or (2) be mounted on and operate on a surface, or (3) move around and operate on a surface.

### 2.1 Machines operating in crystalline solid state

Garcia-Garibay and co-workers have made major progress in the formulation, design, and preparation of crystalline molecular machines.<sup>22</sup> Experience gained from their work on molecular "compasses" and "gyroscopes"<sup>23,24</sup> formulated several important concepts including "amphidynamic crystals." Unlike conventional crystalline materials, in which molecules are held tightly together and no substantial motion is allowed, amphidynamic crystals accommodate high molecular mobility of the moving parts of a molecular machine within a rigid crystal framework. It is anticipated that the successful implementation of such crystalline states will yield new photonics materials. This is an interesting branch in molecular machine development because optoelectronics applications require a high density of active components that cannot be achieved from highly diluted forms in solution or from thin layers on a surface.



**Jason Matthew Guerrero**

*Jason Matthew Guerrero was born in Corpus Christi, Texas where he went on to receive his BS from Texas A&M University, Corpus Christi. He worked as an undergraduate research assistant as a Welch Foundation and Alliance for Minority Participation fellow under the direction of Professor Eugene Billiot. He then received his MA in 2005 from Rice University where he is currently a PhD candidate working on the development of motorized nanocars under the direction of Professor James Tour.*



**James M. Tour**

*James M. Tour, a synthetic organic chemist, received his BS in chemistry from Syracuse University, his PhD in synthetic organic and organometallic chemistry from Purdue University, and post-doctoral training at the University of Wisconsin and Stanford University. After 11 years at the Department of Chemistry and Biochemistry at the University of South Carolina, he joined the Center for Nanoscale Science and Technology at Rice University in 1999 where he is the Chao Professor of Chemistry, and Professor of Computer Science, and Mechanical Engineering and Materials Science. He is also Director of the Carbon Nanotechnology Laboratory.*

## 2.2 Machines mounted and operating on a surface

The positioning of molecule-sized machines on a surface is the first step toward being able to pump, push, or lift materials, generating useful work. Several types of surface mounted molecular machines such as altitudinal<sup>25</sup> and azimuthal<sup>5b</sup> rotors, cyclodextrin necklaces,<sup>26</sup> molecular muscles,<sup>27</sup> and molecular shuttles<sup>28</sup> have been prepared and assembled on surfaces. The unidirectional molecular motor, whose operation had been demonstrated only in the solution state, was recently extended to the surface mounted motor.<sup>29</sup> Furthermore, a sound approach to the problem of interfacing with surroundings was demonstrated by incorporating light powered molecular motors into a liquid crystal film.<sup>30</sup> In this example, rotation of a microscopic glass rod ( $5 \times 28 \mu\text{m}$ ) on the liquid crystal film was observed using an optical microscope, and its direction of rotation was determined by the helicity of the molecular motor within the film. The work clearly demonstrated that a collective change in the motor-containing liquid crystal film can be used to rotate microscopic-scale objects by harvesting light energy, and that a rotary molecular motor can perform work.

## 2.3 Machines moving and operating on a surface

Unlike most molecular machines that are mounted and operated on a surface in a collective manner, the confirmation of the movement of machines laterally on surfaces, accomplishing some mechanical task, make the use of scanning probe microscopy (SPM) techniques indispensable. This adds difficulties to the experimentation as well as the molecular design,<sup>31</sup> since the molecules must be imaged by the instrument. Nevertheless, in the last decade the use of SPM techniques, specifically scanning tunnelling microscopy (STM), have culminated in the ability to manipulate individual molecules with atomic-scale precision.<sup>32,33</sup> The controlled lateral translation of single molecules on surfaces has been demonstrated using a wide variety of molecules such as Cu-TBP-porphyrin,<sup>34</sup> C<sub>60</sub>,<sup>35,36</sup> the molecular lander,<sup>37</sup> molecular wheelbarrow,<sup>38</sup> nanowalker,<sup>39</sup> HB-DC (hexa-*tert*-butyl decacyclene),<sup>40</sup> HB-HPB (hexa-*tert*-butyl hexaphenylbenzene),<sup>41</sup> and nanocar.<sup>42</sup>

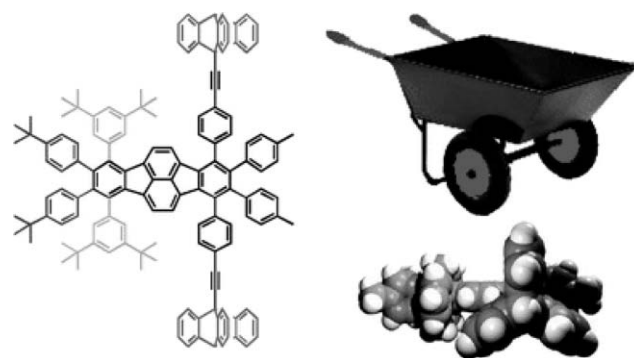
The motion of an object on a variety of surfaces is determined or controlled by the mechanical interactions between the object and the surface. For macroscopic objects, we know the theory and basic rules for the design of machinery to control such mechanical interactions. For instance, we know that skiing is efficient on surfaces such as snow-covered ground or ice, whereas the use of wheels for locomotion is probably not a good choice for those surfaces. On the surface of water, rolling with wheels may not be the best choice; sailing with a ship or boat could be more efficient. These situations are trivial and easy to imagine, yet still require complex theories and rules to describe them mathematically and physically. In contrast, if the size of the object were reduced to several nm across, which correspond to the size of a single molecule, problems arise in attempting to develop theory and basic rules that apply. It is no longer intuitive for most people and not possible to imagine efficient machinery.<sup>43</sup> Movement on surfaces might not follow Newtonian physics; only quantum mechanics might be more predictive,<sup>44</sup> but it can be

quite difficult and computationally expensive to obtain exact answers with the currently available tools. Thus, for the further development of functional molecular machinery that can move and operate on surfaces, it is indispensable to try many different conditions and accumulate enough results that can lead us to the next step of the rational design of functional molecular devices.

## 3. Development of surface-rolling molecules

Because of the limitations of current tools for nanoscience, a detailed single-molecule study on a surface is limited to atomically flat solid surfaces that are suitable for SPM observational techniques.<sup>32,33</sup> Consequently, the test bed for surface-capable molecular machines will be atomically flat surfaces. The most intuitive machinery for controlled translations on such surfaces would be a nanovehicle with molecular wheels, similar to our everyday experiences. Although quantum mechanics might not predict wheels as the best choice on the nanoscale,<sup>43</sup> it would also be difficult to disprove their efficiency without actual testing. The wheelbarrow (Fig. 1)<sup>6,31,38</sup> was one of the first molecules that was actually designed to address the mechanics of rolling wheels and motion at the nanoscale.

We embarked on the project of constructing surface-rolling molecules about eight years ago to further extend the development of nanomachines that can move and operate on a surface. The goal of the project was to realize a nanomachine that can convert energy-inputs (such as heat or electric fields) into controlled motion on a surface and transport of nanocargo (materials or information) from one place to another on the surface. This will be an important step toward future nanomachine development because the bottom-up constructions will, in part, take place on the surface of semiconductors, metals, or biological and artificial membranes. Thus, gaining better data regarding the chemistry and physics acting on molecular scale transporters on a surface is critical, and the surface-rolling nanovehicles (nanocars and nanotrucks) give us opportunities to learn some basic rules for their design and operation. The progress toward this goal in our laboratories is summarized in Fig. 2, beginning with the original nanotruck and ending with the very recent achievements on the synthesis



**Fig. 1** Molecular structure of a molecular wheelbarrow (left), side view of the CPK model (bottom right), and its macroscopic analogue (top right). (Reproduced from ref. 45 with permission. Copyright 2005 Royal Society of Chemistry.)



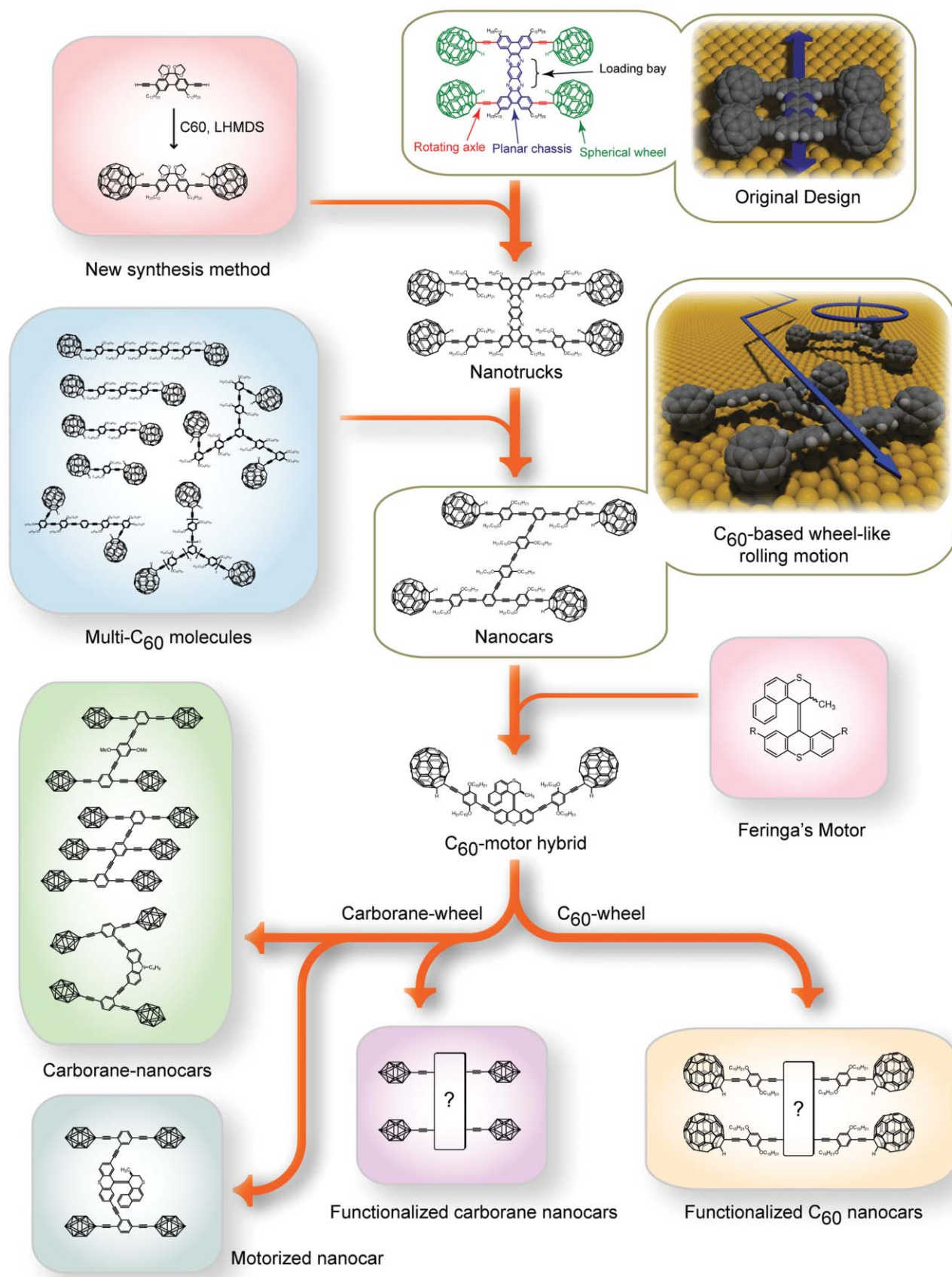
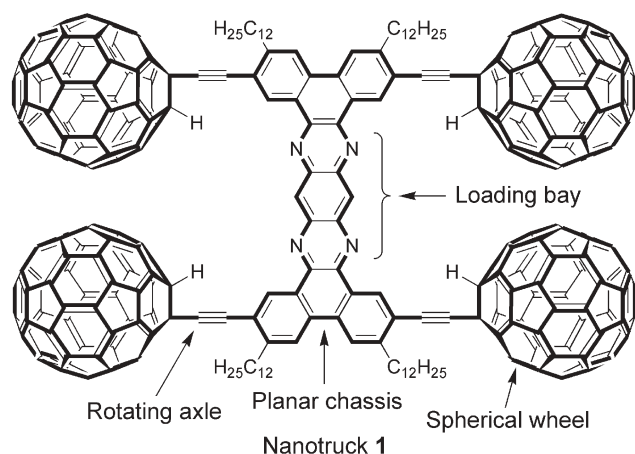


Fig. 2 Development of surface-rolling molecules.



**Fig. 3** The structure of the original nanotruck. (Reproduced from ref. 50 with permission. Copyright 2006 American Chemical Society.)

of motorized nanocars, carborane-wheeled nanocars, and other future generation structures.

At the outset, a definition of terms is helpful since we are defining names of single-molecule entities by analogy to the macroscopic view of vehicles, namely cars and trucks. As with any analogy, there are similarities and dissimilarities between the entities of comparison; if there were no dissimilarities the two entities would no longer be analogous. The highest-level formal definition of a vehicle is “any device on wheels for transporting people or objects.”<sup>46</sup> We demonstrate here a nano-sized “device on wheels for transporting” itself (*ca.* 100 nm, as recorded), and on that basis we use the term “nanocar”, albeit obviously displayed with dissimilarities from the common macroscopic objects. Likewise, a truck is a “vehicle for hauling loads,”<sup>46</sup> and when we constructed a nano-sized “device on wheels” that has a platform that might accommodate a load, we used the term “nanotruck”.

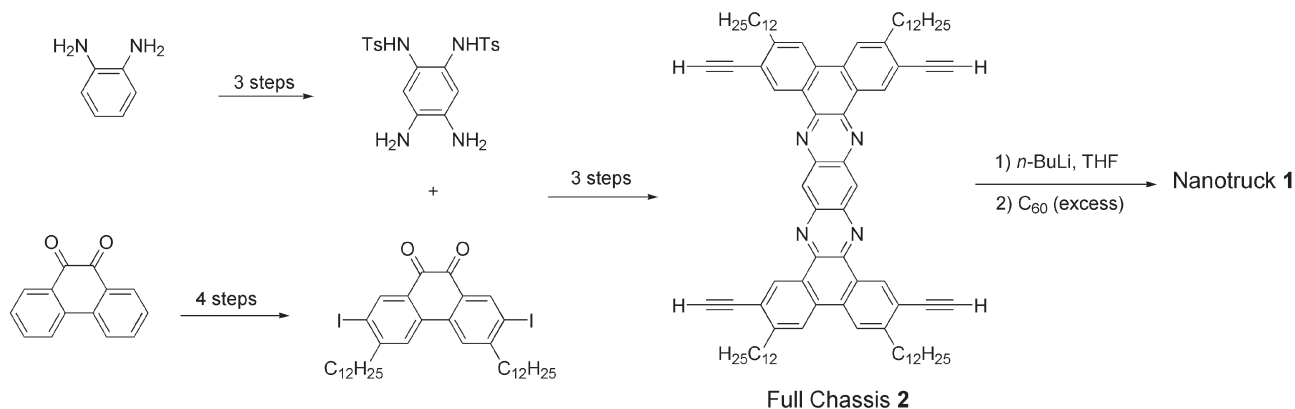
### 3.1 First generations of nanovehicles: nanotrucks

The detailed structure of the first surface-rolling molecule, nanotruck **1**, is shown in Fig. 3, which was designed roughly eight years ago in our laboratory and synthesized up to the full-chassis **2**, to which the fullerenes could be attached (Scheme 1).<sup>47</sup> We chose to use fullerene as the wheels because of its perfect spherical structure; unfortunately, we found the

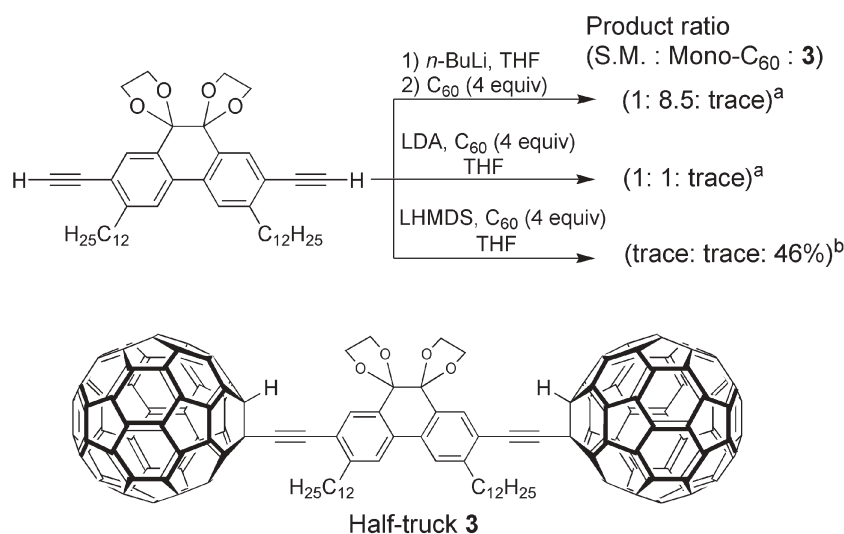
synthesis of fullerene derivatives to be synthetically challenging. In fact, the final reaction step of attaching four fullerenes proved to be quite demanding.<sup>48</sup> It was not until several years later that we learned the insolubility of the structures similar to **1**; isolating the pure product proved to be difficult. Furthermore, the model study with the half-truck **3** (Scheme 2) showed that the standard ethynylation procedure (fullerene–triple bond forming reaction)<sup>49</sup> was not effective enough to attach multiple numbers of fullerenes.<sup>50</sup> The *in situ* ethynylation procedure,<sup>51</sup> in which multiple numbers of terminal alkynes are deprotonated in THF using excess lithium hexamethyldisilazide (LHMDS) in the presence of excess fullerenes, was eventually required for the successful reactions (Scheme 2). This new reaction was quite effective, and applied to the range of multi-fullerene molecules (Fig. 2) as well as the original nanotruck **1**. Because **1** was insoluble, the formation of the product was confirmed by solid-state characterization techniques including MALDI mass spectrometry and NMR.<sup>50</sup> The solubility of the original structure **1** was, however, improved later by incorporating the long alkyl chains ( $-\text{OC}_{12}\text{H}_{25}$ ) as solubility enhancers, and this modification resulted in the successful formation of the nanotruck **4** (Scheme 3)<sup>50</sup> whose structure was determined using common solution state spectroscopy methods. Through the syntheses of several related molecular structure versions, it was clear that the alkyl units were critical for the requisite solubility of these multi-fullerene structures. These highly flexible groups have minimal interactions with surfaces, compared to the strong charge transfer interaction of the fullerene-wheel on gold.<sup>52</sup> The molecule–surface interaction is likely to be dominated by the characteristics specific to the fullerene wheels on gold surfaces; the alkyl groups contribute comparatively little to the surface stiction.

### 3.2 The first successful nanovehicle: nanocar<sup>42</sup>

It was not until the development of the nanocar **5** and its three-wheeled relative **6** (Scheme 4) that we were able to demonstrate the first example of wheel-assisted rolling motion, not the common stick-slip or sliding translation, at the single molecular level using STM. The evidence for the fullerene-wheel-assisted rolling motion was obtained by the comparison of two different modes of thermally induced motions (*via* heating of the gold substrates): translation for **5** (Fig. 4a) and



**Scheme 1** Final synthesis step toward the original nanotruck **1**.



**Scheme 2** New synthesis method: *in situ* ethynylation of C<sub>60</sub>. <sup>a</sup>Yield determined by <sup>1</sup>H NMR. <sup>b</sup>Isolated yield.

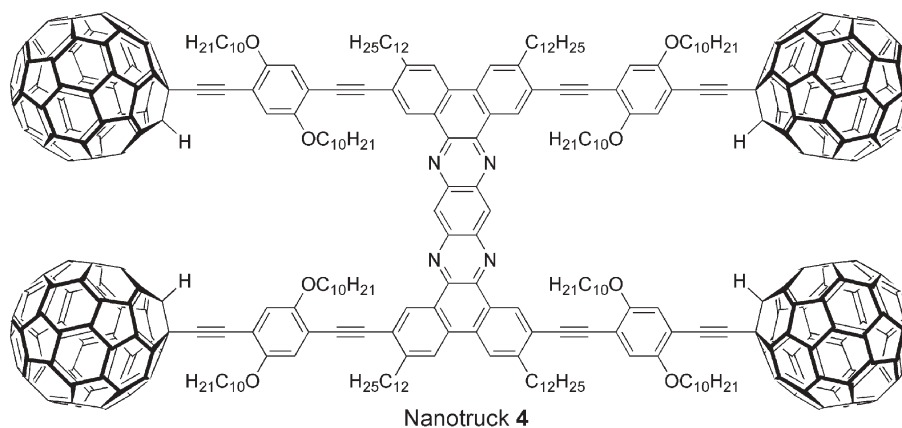
pivoting for **6** (Fig. 4g).<sup>50</sup> Furthermore, motion could be observed by placing the STM tip in front of the nanocar, which would induce rolling motion toward the tip as the tip was moved across the surface.

The key improvement in the molecular structure over the nanotrucks **1** and **4** was the introduction of a semi-rigid chassis as depicted in Fig. 5. With this design change, the possibility of carrying a molecular cargo was lost due to the absence of nitrogen atoms for docking carrier molecules, hence we named the molecule nanocar instead of nanotruck. Compared to the nanotruck chassis structure based on the fused aromatic ring system, the better flexibility of the oligo(phenylene ethynylene) (OPE) chassis combined with the increased number of alkyl units (OC<sub>12</sub>H<sub>25</sub>) dramatically increased the processibility of the massive fullerene-wheeled structures. These improvements eliminated several issues such as the contamination of the sample with pristine fullerenes and possible decomposition of the nanotrucks on gold surfaces during the imaging process. Furthermore, the rotation around the alkyne connections between the chassis and axle portions in the OPE system can cause the molecule to act in a fashion similar to an actual automobile suspension, giving the nanocar flexibility

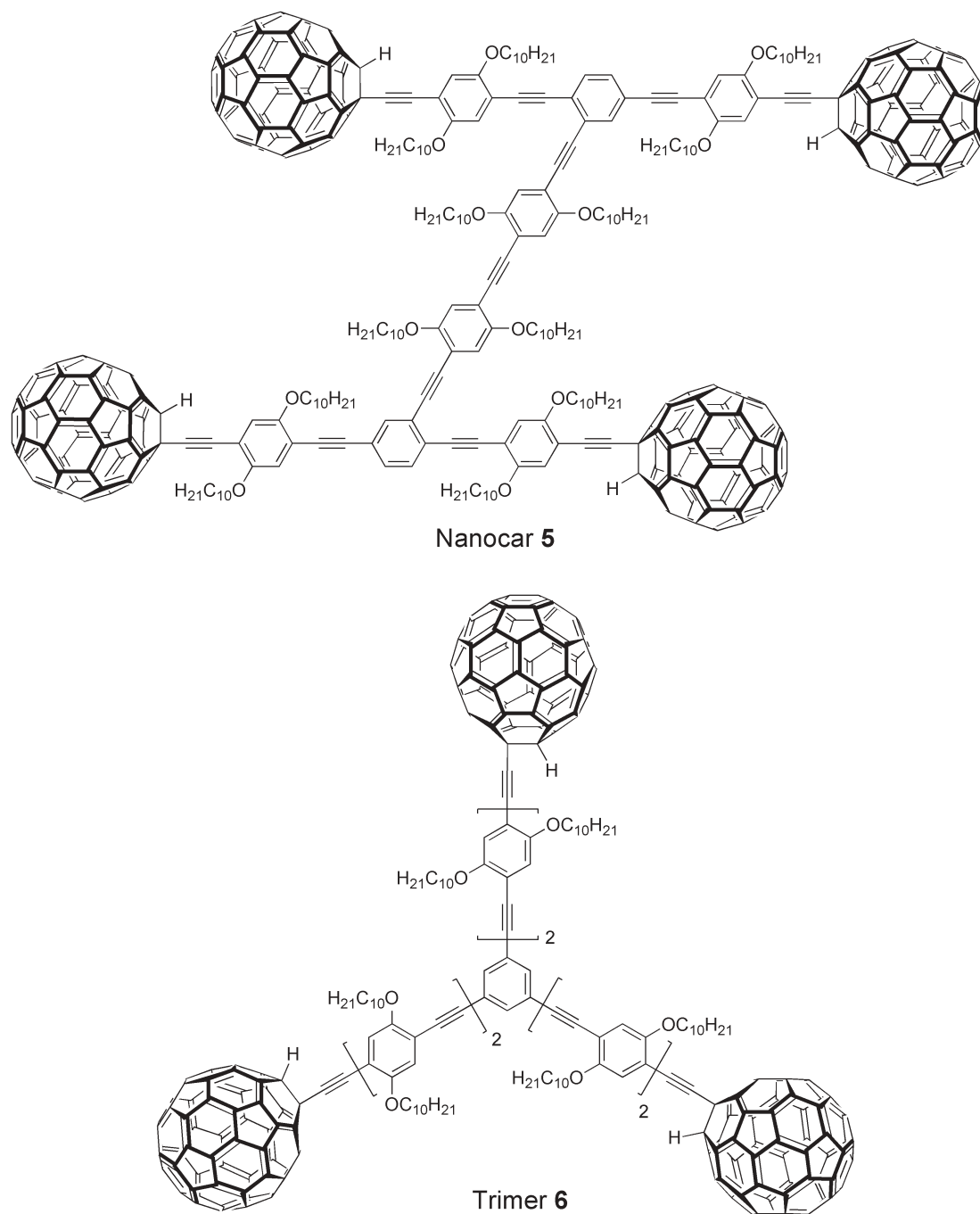
orthogonal to the surface plane, and thereby permitting it to climb one-atom-step high gold islands.<sup>53</sup>

### 3.3 Further development of nanocars: motorization<sup>54</sup>

The achievement with the nanocar **5** was significant because it demonstrated for the first time structurally controlled directional movement on a surface due to rolling of the wheels rather than the common non-directional stick-slip motion of molecules on a substrate surface. The next goal of our project was to realize a nanomachine that can convert energy-inputs into controlled motion on a surface. Nanocar **5** delivered a partial answer to the question of how to control motion on a surface using thermal energy as the energy input. Moreover, we were able to use the electric field of the STM tip to pull the nanocars in a rolling motion forward.<sup>42</sup> Next, we targeted the construction of a motorized nanocar to achieve our project goal. The motorized nanocar bears a light-powered molecular motor in its central portion for an eventual paddlewheel-like propulsion action along a substrate surface for motion of the nanomachine (Fig. 6). We opted to utilize the unidirectional molecular motor (Fig. 2) developed by Feringa and co-workers



**Scheme 3** Nanotruck with solubility enhancing axles.



**Scheme 4** The structure of nanocar **5** and its three-wheel analogue **6**.

as the engine for our motorized nanocar because it can (1) perform repetitive rotary movement, (2) use light and mild heating (35–65 °C) as the power input, (3) precisely perform unidirectional rotation, (4) be functionalized without disturbing rotation allowing the motor substructure to be introduced into more complex structures and (5) operate even when assembled atop metal surfaces.<sup>29</sup>

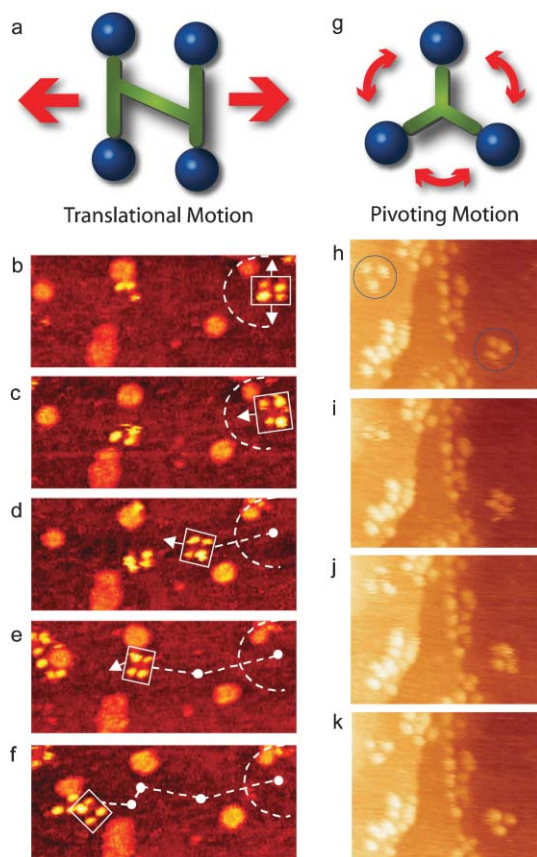
### 3.4 C<sub>60</sub>-motor hybrid and introduction of *p*-carborane wheels

We first sought to incorporate the motor into **5**, however, the model study with the fullerene–motor hybrid **7** (Scheme 5)

revealed the incompatibility of the two molecular components, the fullerene wheel and light-powered motor moieties. The rapid intramolecular quenching of the photoexcited state of the motor moiety by the fullerene wheels mitigated motor operation. Thus, photochemically inert molecular wheels were needed for the development of motorized nanocars.

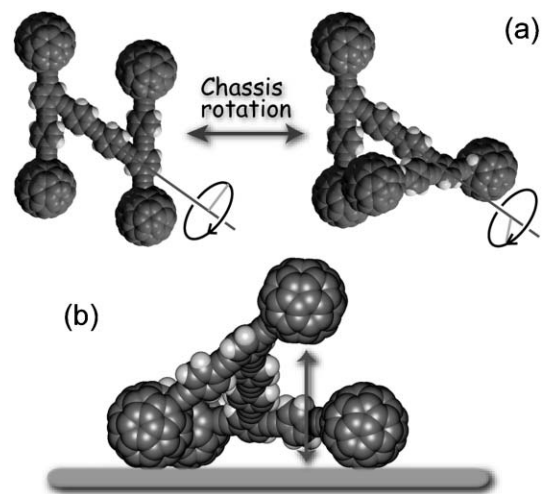
After a survey for alternative molecular wheels, we arrived at the *p*-carborane structure (Fig. 7). The *p*-carboranes proved to be excellent replacements for fullerene wheels because they do not have a strong absorption at 365 nm (the motor's operational wavelength) and they will not quench the motor's photochemical rotary process. Interestingly, both carborane



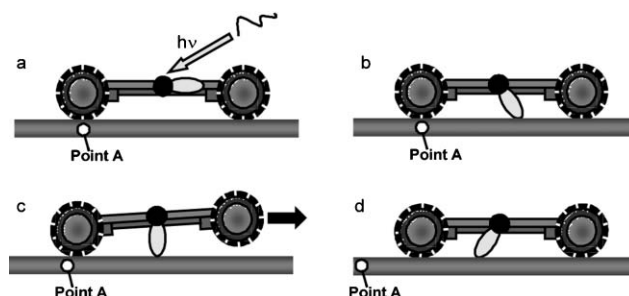


**Fig. 4** Comparison of thermally induced motions of (a) four-wheeled **5** and (b–f) its STM-imaged motions, and (g) three-wheeled **6** and (h–k) its STM-imaged motions. (b–f) Sequence images were taken during annealing at  $\sim 200^\circ\text{C}$  (bias voltage  $V_b = -0.95\text{ V}$ , tunneling current  $I_t = 200\text{ pA}$ . Image size is  $51 \times 23\text{ nm}$ ). The orientation of the nanocar **5** is easily determined by the fullerene wheel separation, with motion occurring perpendicular to the axes.<sup>42</sup> Acquisition time for each image is approximately 1 min, with (b–f) selected from a series spanning 10 min, which shows  $\sim 80^\circ$  pivot (b) followed by translation interrupted by small-angle pivot perturbations (c–f). (h–k) A sequence of STM images acquired approximately 1 min apart during annealing at  $\sim 225^\circ\text{C}$  show the pivoting motion of **6** (both circled molecules) and lack of translation of any molecules. ( $V_b = -0.7\text{ V}$ ,  $I_t = 200\text{ pA}$ . Image size is  $34 \times 27\text{ nm}$ ). For video files of nanocar motions, see: <http://tourserver.rice.edu/movies/>. These figures and experimental text were adapted from our earlier publications,<sup>42,50</sup> and used with permission from the American Chemical Society.

and fullerene share similar properties such as high symmetry ( $I_h$  and  $D_{5h}$ , Fig. 7) and spherical aromaticity,<sup>55</sup> which could be important factors for a molecular wheel. *p*-Carborane is also very robust and, unlike fullerene, highly soluble in common organic solvents, providing advantages in the synthesis of more elaborate surface-rolling nanomachines. Furthermore, the carbon atoms of *p*-carborane can be easily substituted,<sup>56</sup> thus it is possible to construct molecular wheels with functionalized “hub caps”. Hence, the incorporation of the *p*-carborane wheel not only circumvents the photochemical dilemma from the fullerene wheels but also provides a logical continuation of our efforts toward surface-capable functional molecular machines.



**Fig. 5** Flexibility of the semi-rigid chassis structure (nanocar derivative,<sup>50</sup> devoid of alkoxy groups for clarity). (a) The triple bonds in the OPE structure can rotate until the fullerene wheels touch one another, which gives the nanocar flexibility orthogonal to the surface plane. (b) One fullerene wheel is elevated while the other wheels remain on the surface to illustrate the suspension concept. (Reproduced from ref. 50 with permission. Copyright 2006 American Chemical Society.)



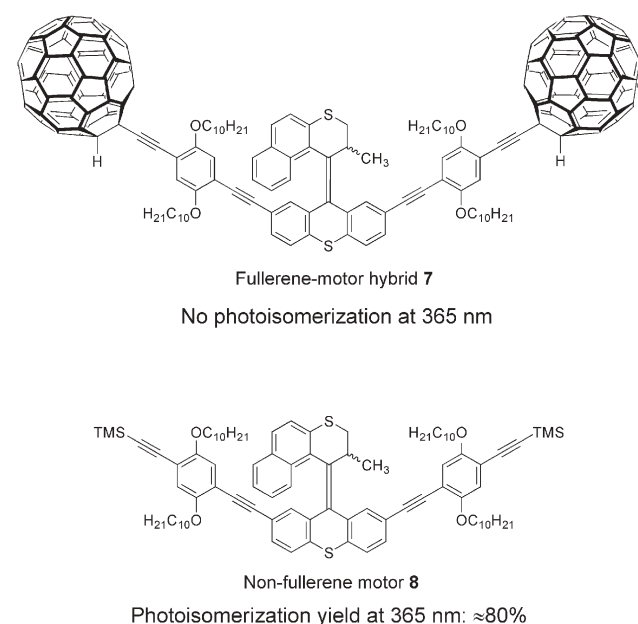
**Fig. 6** Propulsion scheme for the motorized nanocar where (a) 365 nm light would impinge upon the motor which (b) affords motor rotation and (c) sweeping across the surface to (d) propel the nanocar forward. (Reproduced from ref. 54 with permission. Copyright 2006 American Chemical Society.)

### 3.5 Construction of the first motorized *p*-carborane nanocar

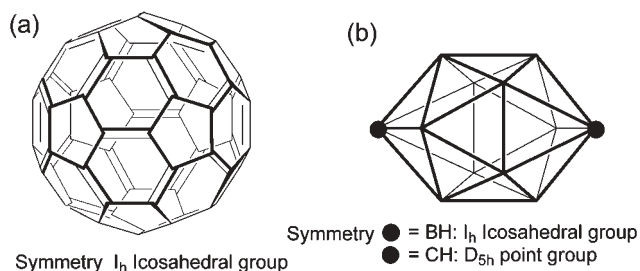
Using the *p*-carborane wheels, we have successfully completed the synthesis of the first motorized nanocar **9** (Fig. 8, and Schemes 6 and 7).<sup>54</sup> There is a noticeable difference between the *p*-carborane (**9**) and fullerene (**5**) containing nanocars besides the existence of the motor moiety. Because of the better solubility of the carborane structure, the final structure is much simpler since the auxiliary solubility groups of **5** ( $\text{OC}_{12}\text{H}_{25}$ ) are not necessary in **9**. Furthermore, the simplicity of the final structures results in the more efficient and rapid synthesis of the nanomachine (Schemes 6 and 7). The motorized nanocar **9** can be synthesized in 12 steps with an overall yield of 5%, whereas the fullerene-based nanocar **5** required at least 14 steps with an overall yield  $<1\%$ . Considering the extra synthesis steps required for the motor moiety, the synthetic advantage gained by the adaptation of *p*-carboranes as wheels is enormous.

Motorized nanocar **9**, due to the symmetrical lower part of the motor, was obtained as a mixture of two pairs of





**Scheme 5** Model study of the fullerene-motor hybrid with and without fullerenes.



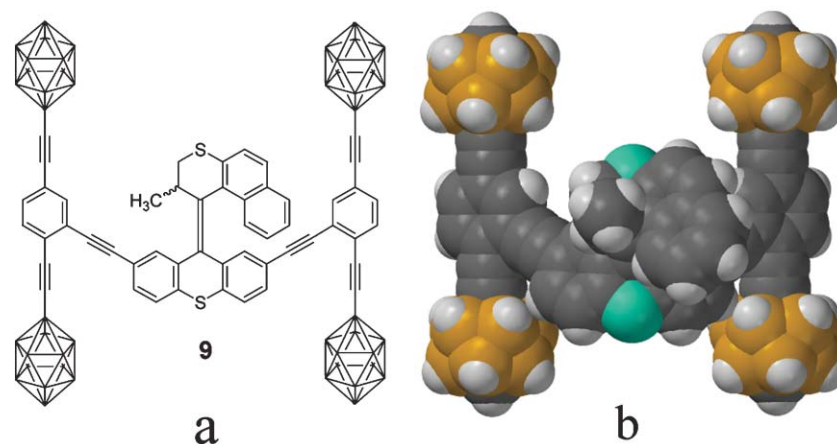
**Fig. 7** The structures of (a) fullerene, (b) *p*-carborane (● = CH), and icosahedral borane cluster (● = BH). All other vertices of the borane cluster have BH units.

enantiomers, meaning that only two motor configurations (stable and unstable) can be detected by  $^1\text{H}$  NMR.<sup>54</sup> Since we expect to address **9** on surfaces as individual entities, every

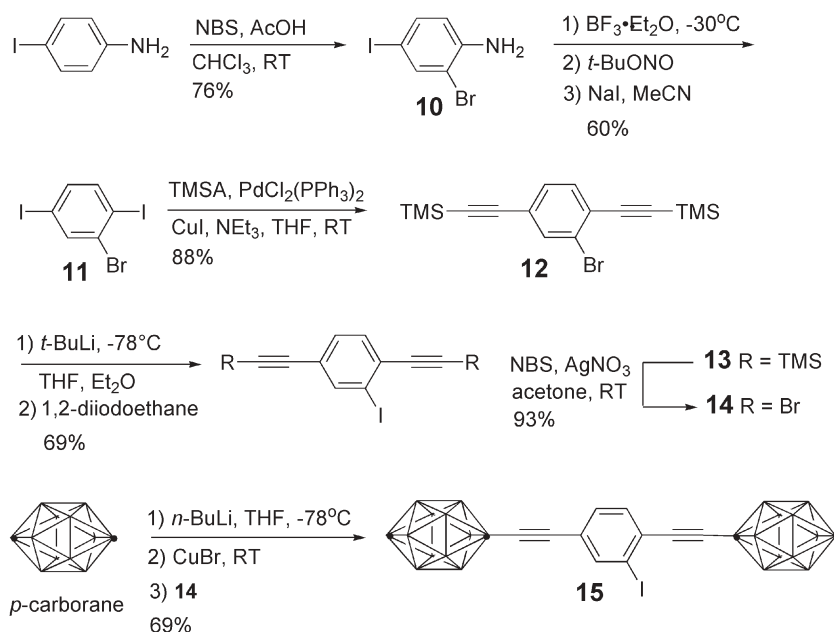
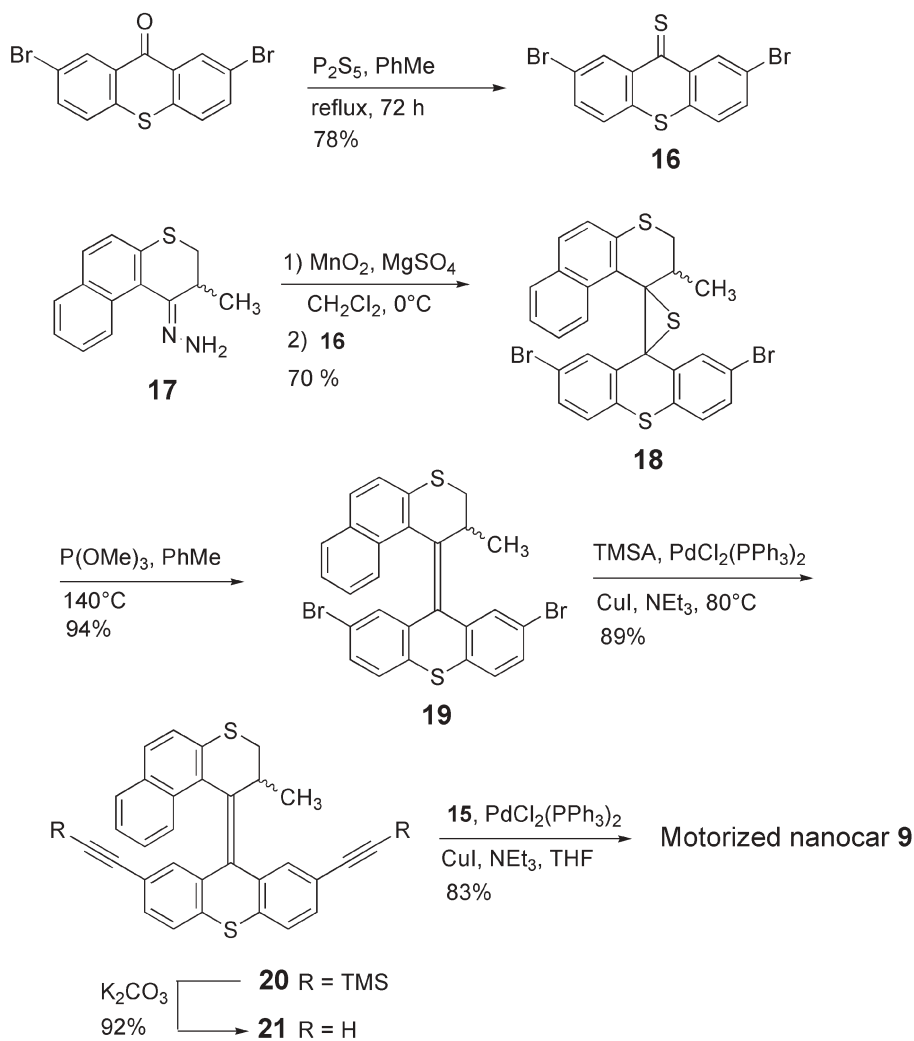
nanocar is homochiral, hence it was unnecessary to resolve the enantiomers. For this reason, we performed kinetic studies in solution by  $^1\text{H}$  NMR on the racemic material.<sup>54</sup> Thermodynamic and kinetic parameters (in solution) of the thermal conversion of the unstable to stable isomer were determined at different temperatures. All the values were similar to those obtained by Feringa for the motor bearing methoxy moieties (rather than alkynes) at the 2,7-positions.<sup>57</sup> Encouragingly, we found that the presence of the relatively bulky *p*-carborane wheels does not alter the rotation of the motor, implying that the chassis and axle-bearing alkynyl moieties are long enough to prevent steric interactions. Finally, whether the motor will have sufficient power to rotate and thus propel the nanocar on a surface remains to be determined using SPM techniques.

### 3.6 Construction of *p*-carborane nanocars

A variety of other carborane-wheeled nanocars and 3-wheeled analogues were rapidly synthesized including **22–25** (Fig. 9). The simplest carborane nanocar **22** was synthesized in seven steps from a common starting material. It would be highly challenging, if possible, to synthesize the fullerene-wheeled version of the nano-caterpillar **23** with as many as six fullerenes. In addition to the simplest nanocar **22**, the nano-caterpillar **23**, curved nanocar **24**, and trimer **25** were designed to aid in the determination of directionality on lateral diffusion of these carborane-wheeled surface-rolling molecules on surfaces using SPM. Thus, the  $3 \times 2$  arrangements of **23**'s wheels will make it possible to determine both molecular direction and diffusion direction by SPM. This is important for the unambiguous determination of the rolling behaviour of these nanovehicles. Because only the wheels are imaged by SPM, **22** is recorded as four bright dots arranged in a square shape, making it impossible to determine the directionality of the molecule from its SPM recorded images. Similarly, the curved nanocar **24** is expected to make small circles on a surface if the molecule is indeed rolling with wheels, and the trimer **25** can be imaged in the same manner as the fullerene trimer **6**. The observation of these drastically different patterns



**Fig. 8** (a) The structure of motorized nanocar **9**. The *p*-carborane wheels have BH at all vertices except at the top and bottom vertices which represent C and CH positions, *ipso* and *para*, respectively, relative to the alkynes. (b) The space-filling model analog of **9**. (Reproduced from ref. 54 with permission. Copyright 2006 American Chemical Society.)

Scheme 6 Synthesis of *p*-carborane-containing axle.

Scheme 7 Synthesis of motorized nanocar 9.

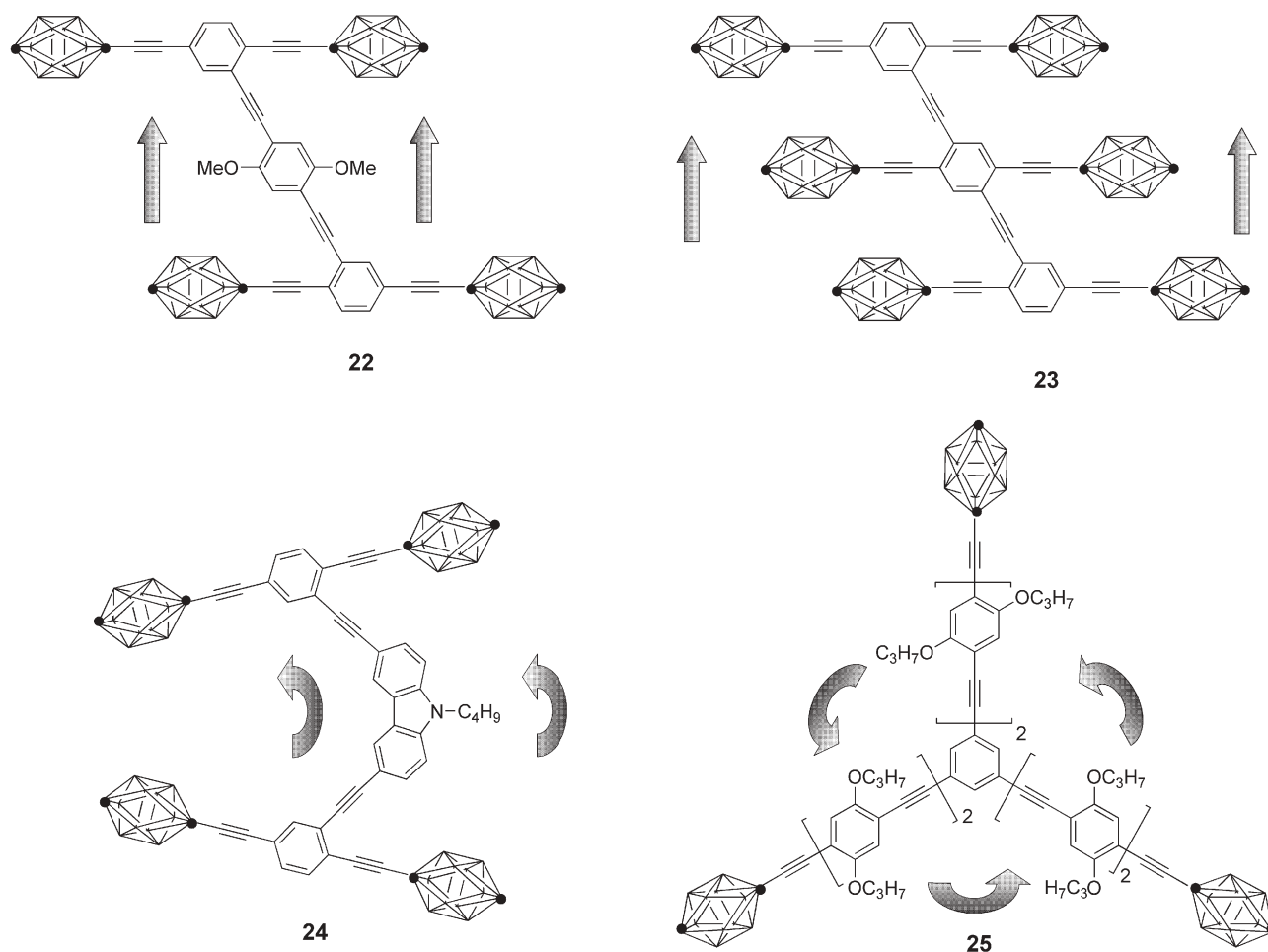


Fig. 9 Molecular structure of *p*-carborane nanocars. The arrows indicate expected direction of rolling motion on surfaces.

of molecular diffusion (rolling) on surfaces will help us to determine the efficacy of the carboranes as molecular wheels.

### 3.7 Functionalized C<sub>60</sub>-wheeled nanocars and other surface-rolling molecules

Unlike the newly introduced *p*-carborane wheels, whose efficacy as molecular wheels is still under investigation using STM techniques, the fullerene wheels are established as an effective wheel component in structure **5** (Scheme 4). It will be fruitful to further develop fullerene-based nanovehicles with some functionality, although the synthesis of such molecules has been challenging. We have targeted the syntheses of additional functionalized fullerene-wheeled nanocars, ranging from a nanocar with a permanent dipole moment, to other porphyrin-based nanotrucks having the capability of carrying molecular cargo and to nanocars with motors that can work in the presence of fullerenes.

We have made similar efforts to synthesize *p*-carborane-wheeled nanocars with comparable functionality. This work is less synthetically challenging than the C<sub>60</sub>-based products, and in fact we have accomplished syntheses of several other prototypes. We are now attempting to prove the rolling *vs.* sliding movement of the *p*-carborane-wheel based vehicles on

surfaces using a variety of microscopy and spectroscopy methods, and this is proving to be the bottle-neck of our current research. This underscores the deficiency in current nano-scale imaging probes, and should encourage the development of these needed tools.

## 4. Conclusions

We have outlined our approach toward the goal of constructing a nanomachine that can convert energy inputs (such as electric fields and light energies) into controlled motion on a surface and transport of nano-cargo (material or information) from one place to another on the surface. The results described here show that the extension of the macroscopic concepts, vehicles with wheels and axles, to the molecular level is of great utility. The novel design of the fullerene wheels provided one answer to the question of how to control molecular diffusion on solid surfaces. The newer *p*-carborane wheel-based nanocars have also been discussed, and their advantages over fullerene structure were clearly evident through the rational design and synthesis of the motorized nanocar and other related structures. However, they are still under investigation using microscopy methods and their efficacy as molecular wheels remains to be determined.



Research continues in our laboratories to further explore the nature of molecule–surface interactions that will shape the future of nanotechnology. It should be noted that currently available surface-capable artificial nanomachines are primitive. It is difficult to predict the practical applications of such molecular machines in the future. Nevertheless, it is also noted that our endeavours in this field have just begun and have been steadily growing both in the number of examples and in the sophistication of each machine produced. Efforts from other laboratories around the world, for example molecular motor development, are proving to provide enhanced components for rapid incorporation into molecular nanomachines. Analytical tools development by groups with that charter are sorely needed in this field, and we eagerly await those further advances. With these complementary efforts, many groups, including our own, will be able to step up the pace of nanomachine development for the world's future technological needs.

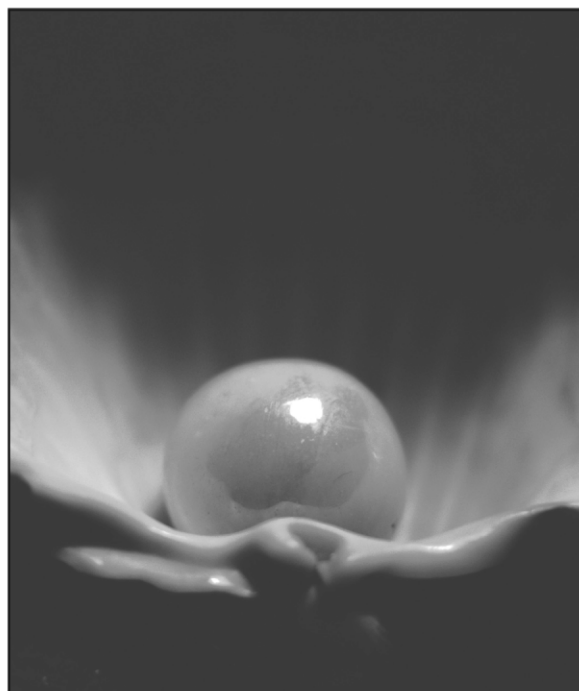
## Acknowledgements

We thank Honda, Zyvex, the NSF (Penn State MRSEC), and the Welch Foundation for funding, and FAR Research (Dr I. Chester) and Petra Research (Dr R. Awartani) for TMSA. J.-F. Morin thanks NSERC and FQRNT for a postdoctoral fellowship.

## References

- 1 T. R. Kelly, H. D. Silva and R. A. Silva, *Nature*, 1999, **401**, 150.
- 2 N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152.
- 3 D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174.
- 4 V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood and J. F. Stoddart, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 1178.
- 5 (a) G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, *Chem. Rev.*, 2005, **105**, 1281; (b) H. Jian and J. M. Tour, *J. Org. Chem.*, 2003, **68**, 5091.
- 6 G. Jimenez-Bueno and G. Rapenne, *Tetrahedron Lett.*, 2003, **44**, 6261.
- 7 T. Muraoka, K. Kinbara and T. Aida, *Nature*, 2006, **440**, 512.
- 8 T. C. Bedard and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 10662.
- 9 J. D. Badjić, V. Balzani, A. Credi, S. Silvi and J. F. Stoddart, *Science*, 2004, **303**, 1845.
- 10 N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage and B. Ventura, *J. Am. Chem. Soc.*, 1999, **121**, 4379.
- 11 A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia and G. W. H. Worpel, *Science*, 2001, **291**, 2124.
- 12 Y. Naorikane and N. Tamaoki, *Org. Lett.*, 2004, **6**, 2595.
- 13 B. E. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, 2001.
- 14 V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines—A Journey into the Nano World*, Wiley-VCH, Weinheim, 2004.
- 15 T. R. Kelly, *Topics in Current Chemistry* 262, Springer, Heidelberg, 2005.
- 16 R. P. Feynman, *Engineering and Science (California Institute of Technology)*, 1960, **23**, 22–36.
- 17 (a) D. K. James and J. M. Tour, *Aldrichimica Acta*, 2006, **39**, 47; (b) D. K. James and J. M. Tour, *Top. Curr. Chem.*, 2005, **257**, 33.
- 18 S. Kawata, H.-B. Sun, T. Tanaka and K. Takada, *Nature*, 2001, **412**, 697.
- 19 B. Li, H. Yu, A. Sharon and X. Zhang, *Appl. Phys. Lett.*, 2004, **85**, 2426.
- 20 (a) For recent reviews on biomolecular machines, see: B. Alberts, *Cell*, 1998, **92**, 291–390 (special issue on macromolecular machines); (b) K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377.
- 21 R. K. Soong, G. D. Bachand, H. P. Neves, A. G. Olkhovets, H. G. Craighead and C. D. Montemagno, *Science*, 2000, **290**, 1555.
- 22 M. A. Garcia-Garibay, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 10771.
- 23 C. E. Godinez, G. Zepeda and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2002, **124**, 4701.
- 24 Z. Dominguez, T.-A. V. Khuong, H. Dang, C. N. Sanrame, J. E. Nuñez and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2003, **125**, 8827.
- 25 X. Zheng, M. E. Mulcahy, D. Horinek, F. Galeotti, T. F. Magnera and J. Michl, *J. Am. Chem. Soc.*, 2004, **126**, 4540.
- 26 H. Shigekawa, K. Miyake, J. Sumaoka, A. Harada and M. J. Komiyama, *J. Am. Chem. Soc.*, 2000, **122**, 5411.
- 27 Y. Liu, A. H. Flood, P. A. Bonvallet, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C.-M. Ho and J. F. Stoddart, *J. Am. Chem. Soc.*, 2005, **127**, 9745.
- 28 J. Berna, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi and F. Zerbetto, *Nat. Mater.*, 2005, **4**, 704.
- 29 R. A. van Delden, M. K. J. ter Wiel, M. M. Pollard, J. Vicario, N. Koumura and B. L. Feringa, *Nature*, 2005, **437**, 1337.
- 30 J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer and B. L. Feringa, *Nature*, 2006, **440**, 163.
- 31 C. Joachim, H. Tang, F. Moresco, G. Rapenne and G. Meyer, *Nanotechnology*, 2002, **13**, 330.
- 32 J. K. Gimzewski and C. Joachim, *Science*, 1999, **283**, 1683.
- 33 F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim and F. Besenbacher, *Prog. Surf. Sci.*, 2003, **71**, 95.
- 34 T. A. Jung, R. R. Schlittler, J. K. Gimzewski, H. Tang and C. Joachim, *Science*, 1996, **271**, 181.
- 35 D. L. Keeling, M. J. Humphry, R. H. J. Fawcett, P. H. Beton, C. Hobbs and L. Kantorovich, *Phys. Rev. Lett.*, 2005, **94**, 146104.
- 36 H. Tang, M. T. Cuberes, C. Joachim and J. K. Gimzewski, *Surf. Sci.*, 1997, **386**, 115.
- 37 F. Rosei, M. Schunack, P. Jiang, A. Gourdon, E. Legsgaard, I. Stensgaard, C. Joachim and F. Besenbacher, *Science*, 2002, **296**, 328.
- 38 L. Grill, K.-H. Rieder, F. Moresco, G. J.-Bueno, C. Wang, G. Rapenne and C. Joachim, *Surf. Sci.*, 2005, **584**, L153.
- 39 K.-Y. Kwon, K. L. Wong, G. Pawin, L. Bartels, S. Stolbov and T. S. Rahman, *Phys. Rev. Lett.*, 2005, **95**, 166101.
- 40 J. K. Gimzewski, C. Joachim, R. R. Schlittler, V. Langlais, H. Tang and I. Johansson, *Science*, 1998, **281**, 531.
- 41 L. Gross, K.-H. Rieder, F. Moresco, S. M. Stojkovic, A. Gourdon and C. Joachim, *Nat. Mater.*, 2006, **4**, 892.
- 42 Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly and J. M. Tour, *Nano Lett.*, 2005, **5**, 2330.
- 43 M. Porto, M. Urbakh and J. Klafter, *Phys. Rev. Lett.*, 2000, **84**, 6058.
- 44 C. Joachim and J. K. Gimzewski, *Struct. Bonding*, 2001, **99**, 1.
- 45 G. Rapenne, *Org. Biomol. Chem.*, 2005, **3**, 1165.
- 46 *Webster's New Twentieth Century Dictionary*, 2nd edn., Collins & World, United States, 1975.
- 47 Y. Yao, *Synthesis of Pyridine-Based Planar Polymers and Nanoarchitectures for Molecular Devices*, PhD thesis, University of South Carolina, 1998.
- 48 H. Yang, *Production of Nanotrucks*, MS thesis, University of South Carolina, 1999.
- 49 K. Komatsu, Y. Murata, N. Takimoto, S. Mori, N. Sugita and T. S. M. Wan, *J. Org. Chem.*, 1994, **59**, 6101.
- 50 Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, C. Yu-Hung, T. Sasaki, J.-F. Morin, J. M. Guerrero, K. F. Kelly and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 4854.
- 51 Y. Shirai, Y. Zhao, L. Chen and J. M. Tour, *Org. Lett.*, 2004, **6**, 2129.
- 52 S. Guo, D. P. Fogarty, P. M. Nagel and S. A. Kandel, *J. Phys. Chem. B*, 2004, **108**, 14074 and references therein.

- 53 Manuscript on detailed STM study is in preparation: A. J. Osgood, Y. Shirai, Y. Zhao, K. F. Kelly and J. M. Tour, *Effect of suspension like behavior can be possibly observed by STM*.
- 54 J.-F. Morin, Y. Shirai and J. M. Tour, *Org. Lett.*, 2006, **8**, 1713.
- 55 Z. Chen and R. B. King, *Chem. Rev.*, 2005, **105**, 3613.
- 56 J. F. Valliant, K. J. Guenter, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein and K. A. Stephenson, *Coord. Chem. Rev.*, 2002, **232**, 173.
- 57 N. Koumura, E. M. Geertsema, M. B. van Gelder, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2002, **124**, 5037.



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