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En Route to a Motorized Nanocar

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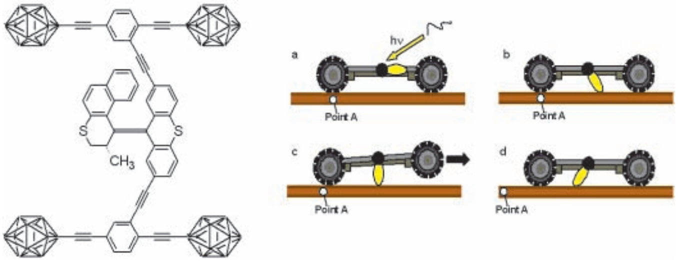
ABSTRACT



With the eventual goal of demonstrating a motorized nanocar, the key structure has been synthesized which bears a light-activated unidirectional molecular motor and an oligo(phenylene ethynylene) chassis and axle system with four carboranes to serve as the wheels. Kinetics studies in solution show that the motor indeed rotates upon irradiation with 365 nm light, and the fullerene-free carborane wheel system is an essential design feature for motor operation.

Recent efforts have been devoted to the synthesis of nanomachines that could perform specific tasks at the molecular level and ultimately construct molecular assemblies using a bottom-up approach.[1] In this regard, the first nanocar bearing a chassis, axles, and fullerene wheels was recently synthesized by our group to exemplify the structurally controlled directional movement on a surface due to rolling of the wheels rather than the common stick−slip motion[2] of molecules on a substrate surface.[3] The motion could be thermally (heated substrate surface) or electrically (STM-tip field) induced, thus opening the way to molecular-structure-defined motion at the nanoscale. We describe here the synthesis of a proposed nanocar that 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 vehicle as shown in Figure 1. Also described is the light-powered behavior, in solution, where the kinetic parameters of motor rotation were measured.

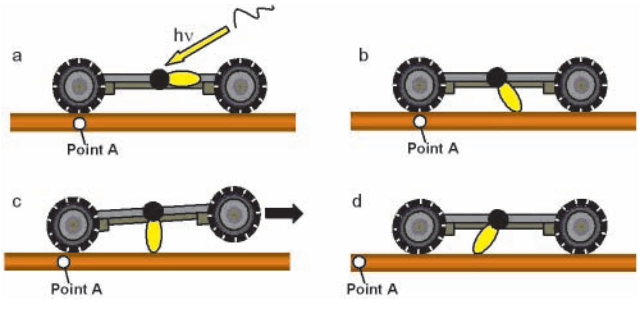


Figure 1. Proposed propulsion scheme for the motorized nanocar **1** where (a) 365 nm light would impinge upon the motor which in conjunction with a heated substrate (at least 65 °C) (b) affording motor rotation and (c) sweeping across the surface to (d) propel the nanocar forward.

Various molecular motors have been developed.[4] Among them, unidirectional motors developed by Feringa et al.[5] are most applicable here because they (i) perform repetitive

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[1] (a) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: A Journey into the Nanoworld*; Wiley-VCH: Weinheim, 2003. (b) Ozin, G.; Manners, I.; Fournier-Bidoz, S.; Arsenault, A. *Adv. Mater.* **2005**, *17*, 13011. (c) Balzani, V. *Small* **2005**, *1*, 278. (d) Kinbara, K.; Aida, T. *Chem. Rev.* **2005**, *105*, 1377. (e) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. (f) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612.

[2] Rosei, F.; Schunak, M.; Jiang, P.; Gourdon, A.; Laegsgaard, E.; Stensgaard, I.; Joachim, C.; Besebbacher, F. *Science* **2002**, *296*, 328.

[3] Shirai, Y.; Osgood, A. J.; Zhao, Y.; Kelly, K. F.; Tour, J. M. *Nano Lett.* **2005**, *5*, 2330.

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rotary movement, (ii) use light and mild heating (35−65 °C) as the power input, (iii) precisely perform unidirectional rotation, (iv) can be functionalized without disturbing rotation allowing them to be introduced into more complex structures, and (v) can operate even when assembled atop metal surfaces. The target nanocar bearing a Feringa motor is shown in Figure 2. Unlike the former nanocar that bore fullerene wheels,[3] we opted for *p*-carborane wheels because we observed that the Feringa motor is completely inoperative in the presence of fullerenes, probably because of rapid energy transfer, prior to rotation, from the excited state of the motor to the fullerenes.[6]

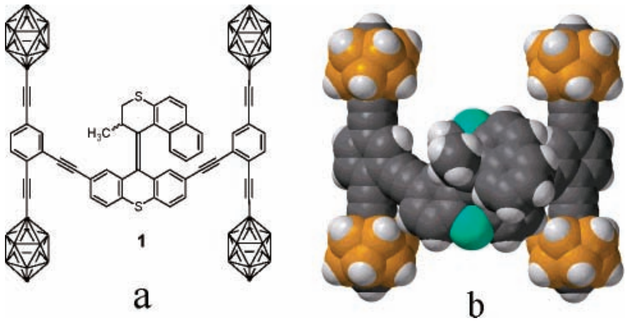
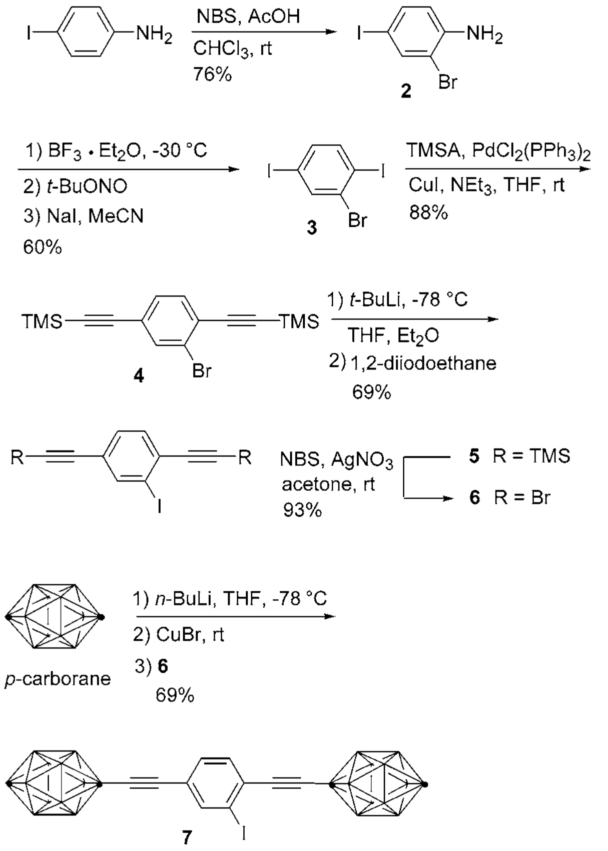


Figure 2. (a) Structure of motorized nanocar **1**. The *p*-carborane wheels have BH at every intersection except at the top and bottom vertexes which represent C and CH positions, ipso and para, respectively, relative to the alkynes. (b) The space-filling model of **1**.

All components of the nanocar **1** were chosen to obtain translational movements on an atomically flat surface allowing surface characterization using scanning tunneling microscopy (STM).[3] First, *p*-carboranes have been used as wheels because they have a three-dimensional, near-spherical structure[7] that does not absorb light at 365 nm[8] which is the motor's operational wavelength, and as we demonstrate here, they do not prematurely quench the motor's photochemical rotary process. Second, alkynes have been used as axles because their energy barrier to rotation is sufficiently low.[3] The synthesis of the motorized nanocar **1** is presented in Schemes 1 and 2.

The axle was synthesized in six steps from 4-iodoaniline (Scheme 1). After bromination to give compound **2**, the amino group was replaced by an iodide using diazonium chemistry followed by iodination to afford **3**.[9] Sonogashira coupling introduced the alkynyl axles. After halogen interconversion (**4** to **5**), in situ desilyl bromination[10] was carried out leading to compound **6** in excellent yield. *p*-Carborane was then coupled to bromoalkyne **6** to afford the axles bearing the two carborane wheels, and no side reaction involving the aromatic iodide was noted at room temperature.

Scheme 1. Synthesis of *p*-Carborane-Containing Axle



To build the motor (Scheme 2), we chose to use the thioxanthene unit as the lower half and a naphtha[2,1-*b*]-thiopyran as the upper half because the resulting motor (unsubstituted) shows a good photostationary state (PSS) ratio at room temperature.[5] Moreover, functionalized thioxanthene can be easily prepared from commercially available 9-thioxanthenone by regioselective electrophilic substitution.[11] Following the Feringa strategy,[5] the thioketone **8** was synthesized by heating 2,7-dibromothioxanthenone[11] in toluene containing phosphorus pentasulfide. The racemic hydrazone **9**[5b] was oxidized to the unstable diazo compound

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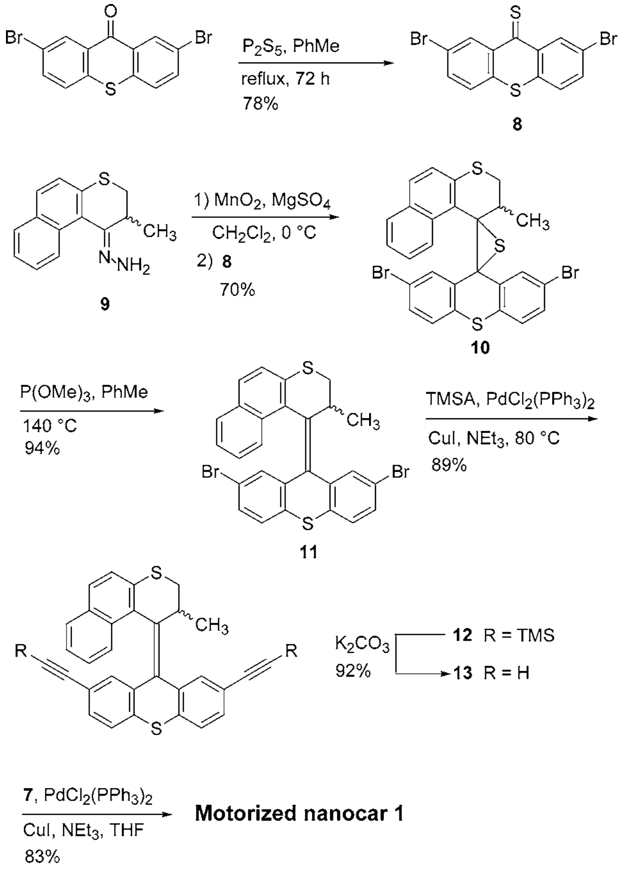
(11) Coleman, M. P.; Boyd, M. K. *J. Org. Chem.* **2002**, *67*, 7641.

Scheme 2. Synthesis of Motorized Nanocar **1**



with activated manganese dioxide in dichloromethane at 0 °C. In our hands, this oxidant gave better results than the silver(I) oxide method formerly used.[5] Thioketone **8** was then added to the diazo compound leading to an isomeric mixture of episulfides **10**. The desulfurization was then accomplished using trimethylphosphite to give **11** in excellent yield. In our case, triphenylphosphine gave only partial conversion to the alkene. This can be attributed to steric hindrance induced by the bromine atoms in the 2- and 7-positions of the thioxanthene unit. The alkynes were introduced using standard Sonogashira couplings with TMSA and then the axle/wheel assembly **7** to give the motorized nanocar **1** in an overall yield of 5% for 12 steps.

Motorized nanocar **1**, because of the symmetrical lower part of the motor, is obtained as a mixture of two pairs of enantiomers meaning that only two motor configurations (stable and unstable) can be seen by ^{1}H NMR (see Supporting Information). As we expect to address **1** on surfaces as individual entities, every nanocar is homochiral, hence it was unnecessary to resolve the enantiomers. For this reason, we can perform kinetics studies in solution by ^{1}H NMR on the racemic material. To avoid any interference with trace solvent or the *p*-carborane-related peaks, we monitored the rotation of the motor in toluene-d_8 using the doublets at 8.01 ppm (stable isomer) and 7.95 ppm (unstable isomer) (see Supporting Information). Before starting the photoisomerization study, the sample was heated in an NMR tube at 65 °C for 3 h to obtain only the thermally stable conformation of the motor. A ratio of >99:1 was thus obtained. The NMR tube was then irradiated at room temperature with a UV lamp using a 365 nm filter at a light intensity of ca. 10 mW/cm^2. The PSS was obtained after 60 min with an equilibrium ratio of 18:82. Increasing the temperature to 65 °C has a dramatic effect on the unstable isomer as shown in Figure 3. At that temperature, 90% of the unstable isomer was converted to the stable isomer after 50 min. This is encouraging for future applications because the motor can be switched on and off over a very short range of temperatures.

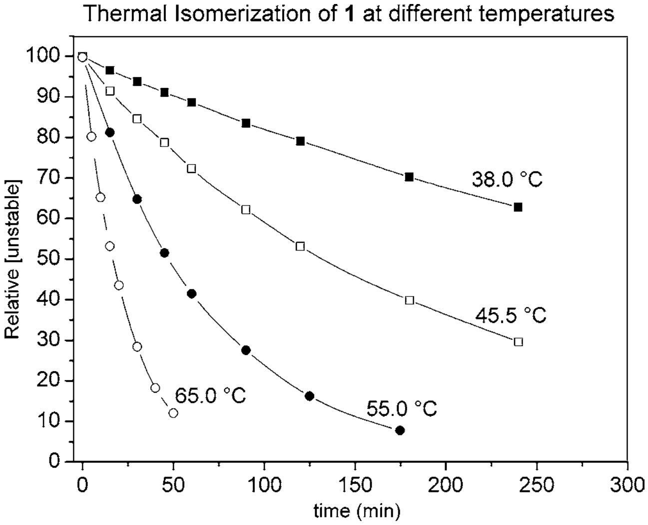


Figure 3. Graph of the relative concentration of the unstable isomer vs heating time at different temperatures.

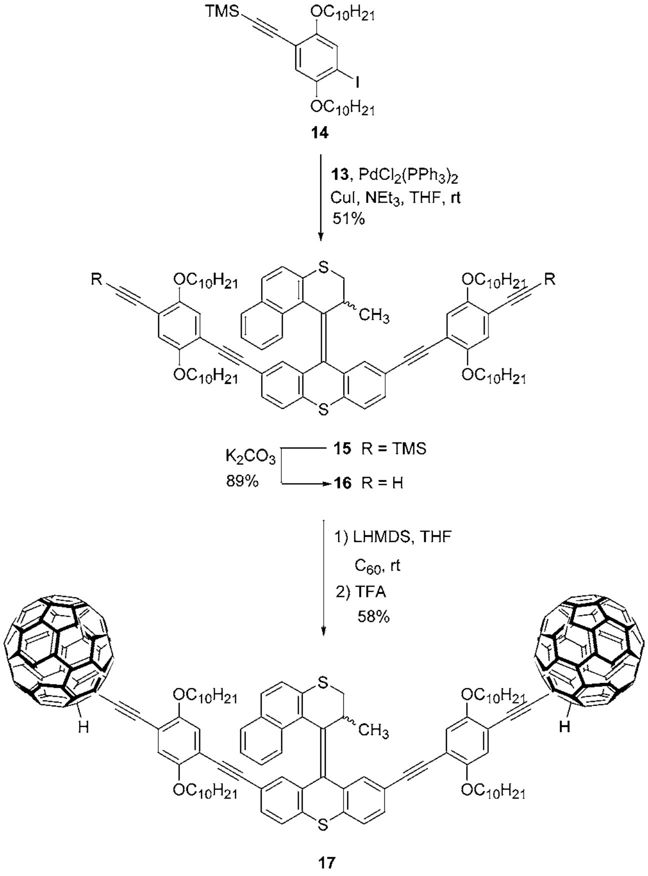
Kinetic parameters (in solution) of the thermal conversion of the unstable to stable isomer have been determined by ^{1}H NMR at different temperatures and are shown in Table 1. All the values are very similar to those obtained by Feringa for the motor bearing methoxy moieties (rather than alkynes) at the 2,7-positions.[5b] Encouragingly, 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. Moreover, the ^{1}H NMR spectrum of **1** in toluene-d_8 remains intact after >10 h of irradiation at 10 mW/cm^2; no significant decomposition products were observed.

Table 1. Kinetic Parameters of Motorized Nanocar **1** in Toluene-d_8 as Determined by ^{1}H NMR

E_a kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ cal/mol K	$\Delta^{\neq}G^{\theta}$ kcal/mol	k^{θ} s^{-1}	$t_{1/2}{}^{\theta}$ h
23.75	23.11	−4.49	24.82	1.91×10^{-6}	101

Finally, to evaluate the influence of the presence of C$_{60}$ (used as wheels in our first nanocar design[3]) on photoisomerization of the motor, we synthesized a system in which the motor is covalently linked to the fullerenes as shown in Scheme 3. To ensure good solubility of the resulting molecule for NMR analysis, a didecyloxybenzene unit needed to be introduced between the motor and the two fullerene moieties. Starting from hydroquinone, **14** was synthesized in three steps as we described previously.[12] Compound **14** was coupled to **13** using standard Sonogashira coupling conditions to give **15**. The alkynes were then deprotected yielding **16**, and fullerenes were introduced using lithium hexamethyldisilazide (LHMDS)[12] with an excess of C_{60} to give **17**.[13]

Scheme 3. Synthesis of C_{60}-Containing Motor



Compounds **15** and **17** were subjected to the same photoisomerization procedure to which nanocar **1** had been exposed. Although **15** underwent ca. 80% conversion upon irradiation for 120 min, no isomerization was detected in **17**. The intramolecular quenching of the photoexcited state of the motor moiety by the fullerene wheels mitigates motor operation. Thus, we cannot use our previous fullerene-wheel-based nanocar design[3] with the Feringa motor; use of the carborane wheels is essential.

Whether energy transfer to the metallic surface during photoisomerization will be problematic needs to be further evaluated. If there is such energy transfer to the metal surface, use of a short alkanethiol monolayer as an insulating barrier, as in Feringa's gold-surface-bound isomerization study,[5a] or change to a nonconductive surface will be necessary; the latter requires a non-STM-based probing technique such as atomic force microscopy or fluorescence microscopy. Furthermore, whether the motor will have sufficient energy to rotate and thus propel the nanocar on a surface remains to be determined.

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Supporting Information Available: Synthetic procedures, ^{1}H NMR, ^{13}C NMR, IR, and mass spectra of compounds **1**, **3**−**8**, **10**−**13**, and **15**−**17** and details of the kinetics study of thermal isomerization of the motorized nanocar. This material is available free of charge via the Internet at http://pubs.acs.org.

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