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Molecular Machinery: Synthesis of a "Nanodragster"

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ABSTRACT

The synthesis and imaging by scanning tunneling microscopy of a mixed wheeled nanovehicle composed of a *p*-carborane small-wheeled short front axle and a C_{60} large-wheeled long rear axle that has been termed a nanodragster due to the structural relation to a dragster are reported. This nanodragster is expected to exhibit motion at a lower temperature than pure C_{60}-wheeled nanocars and should allow the investigation of the role played by *p*-carborane wheels in directional motion.

The recent development of probe microscopy techniques, in particular, scanning tunneling microscopy (STM), has allowed the manipulation and imaging of individual molecules with atomic-scale precision.[1] These new techniques have expanded the field of molecular machinery from the more traditional solution-based machines[2] to the design and synthesis of molecular machines that are individually addressable or controllable. The controlled lateral manipulation by the STM tip of single molecules on surfaces has been demonstrated with a wide variety of molecules such as Cu(II)-*meso*-*tetrakis*-(3,5-di-*tert*-butylphenyl)porphyrin (Cu-TBPP),[3] C_{60},[4] a molecular lander,[1c] a molecular wheelbarrow,[5] hexa-*tert*-butyl-decacyclene (HB-DC),[6] and the molecular rack and pinion.[7] However, only a few studies have been described on the rolling versus sliding motion of what

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could be called molecular wheels.[8] Molecules showing wheel-like rolling motions should facilitate the understanding of the basic concepts of nanomachinery, leading to more complex functionality in molecular vehicles with varying properties.

We have recently developed a family of nanovehicles designed to operate on surfaces and to be studied at the single-molecule level.[9] These so-called nanocars are composed of a chassis connected to wheel-terminated axles and are designed to convert energy inputs such as heat, electric fields, or light into controlled motion on a surface. The nanocar wheels are designed to induce a directional motion of the nanocars on a surface. C_{60} fullerenes were the first wheels used, and they allowed the STM demonstration of a directional rolling mechanism of a nanocar on a gold surface.[8a] However, the C_{60}-based nanocars[10] require an elevated temperature (~200 °C) to initiate motion due to the strong interaction between the fullerene wheels and the gold surface of ~2 eV per wheel.[8a] In addition, the low solubility of the fullerene-wheeled nanocars and the incompatibility of the fullerene with photochemical processes necessitated the development of new *p*-carborane[11] and ruthenium-based wheels.[12] However, *p*-carborane-wheeled nanocars are more difficult to image at room temperature due to their much weaker interaction with metallic surfaces.

Even though we recently observed directional motion of *p*-carborane-wheeled nanocars on glass surfaces by single molecule fluorescence microscopy,[13] such behavior has not yet been reported on a metallic surface where single-molecule features are observed. Despite a large number of reported nanovehicles using C_{60}, *p*-carborane, or ruthenium-based wheels,[9] no example of mixed-wheeled nanovehicles has been reported. By combining C_{60} and *p*-carborane wheels on a single nanocar chassis, we expect to take advantage of the charge transfer interaction between the C_{60} wheels and the gold surface[14] and the weaker physisorption of the *p*-carborane wheels to the gold, to study the motion at lower temperatures than pure C_{60}-wheeled nanocars. Furthermore, this model should allow the investigation of the role of *p*-carborane wheels in directional motion by STM. We report here the synthesis and initial imaging of a mixed-wheeled nanocar combining C_{60} and *p*-carborane wheels that we term a nanodragster due to its structural similarity to macroscopic dragsters: small front wheels on a short axle and large rear wheels on a longer axle.

Nanodragster **1** (Figure 1) was synthesized by first connecting a *p*-carborane-wheeled axle to the chassis. Then,

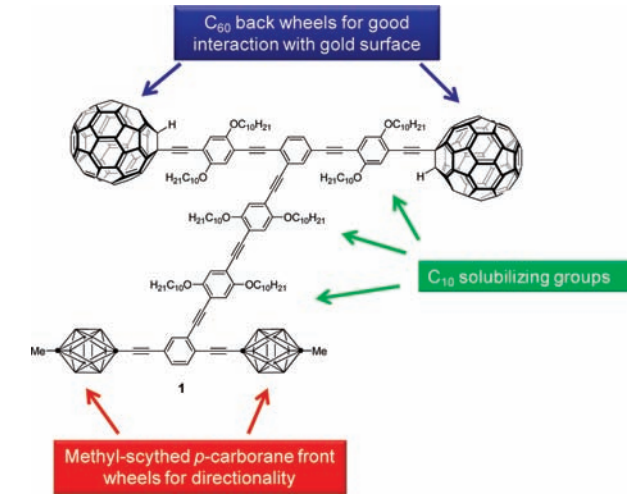

Figure 1. Design of nanodragster **1**. The *p*-carboranes have BH at every intersection except at the points denoted by (●) which represent C positions.

a second axle was appended, and finally two C_{60} wheels were added. Methyl-scythed-*p*-carborane wheels were used to avoid the deprotonation of the CH proton of the *p*-carborane moiety during the C_{60} connection step. The inner chassis was composed of a two-ring phenylene-ethynylene (**2**)[15] substituted by long alkyl chains to ameliorate the poor solubility of the final product. Using the previously reported carborane axle **3**[11a] and the chassis **2**, they were coupled by a Sonogashira reaction (Scheme 1). The *p*-carborane wheels were subsequently C-methylated by reaction with *n*-butyllithium followed by quenching with iodomethane.[16] The intermediate **5** was deprotected with TBAF and coupled to the junction **7**[11a] to yield **8** after deprotection. To easily differentiate the two axles by STM and to increase the solubility of the final compound, the C_{60}-wheeled axle was extended by two ethynylphenyl units. **10** (Scheme 2) was

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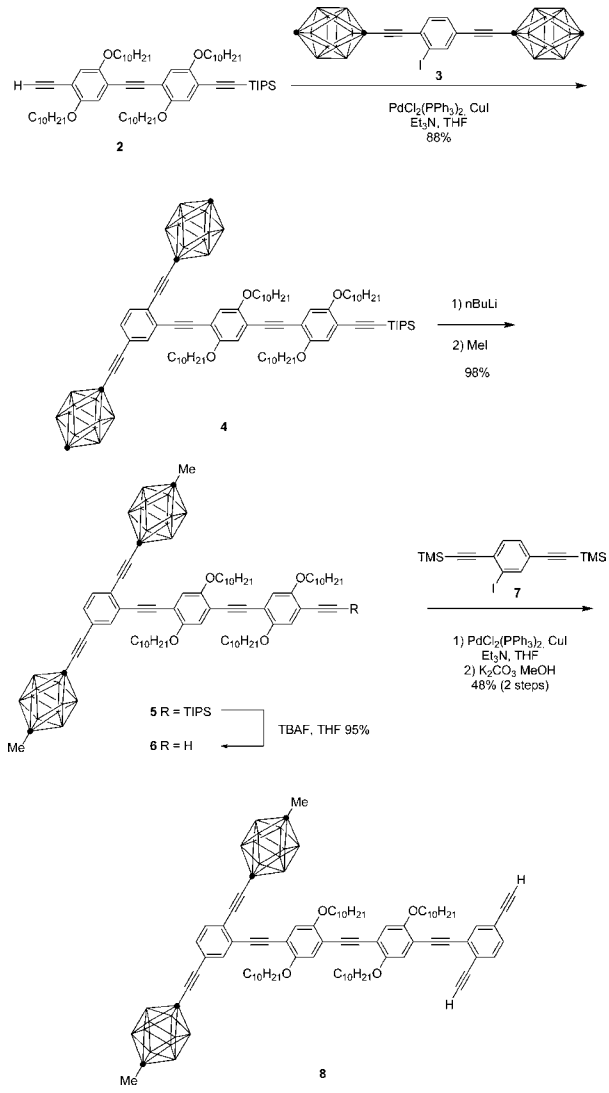
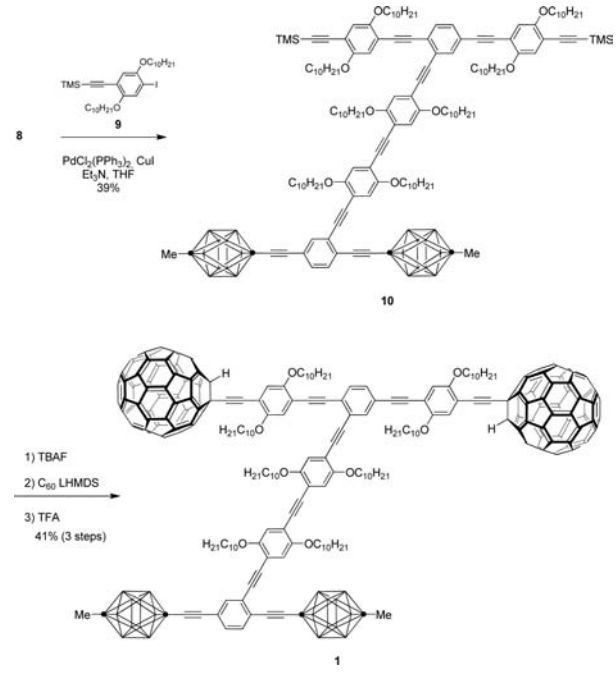
Scheme 1. Synthesis of the Chassis and Front Axle Wheel Units



thus obtained by a double Sonogashira coupling between **8** and **9**.[10a] **10** was deprotected and subjected to the in situ ethynylation reaction[15] with excess LHMDS and C_{60} to yield **1** in a 41% yield. Thanks to the $C_{10}H_{21}$ solubilizing groups, nanodragster **1** shows good solubility in common solvents, allowing full characterization by the standard techniques including ^{1}H and ^{13}C NMR, FTIR, and mass spectrometry.

The nanodragster molecules were imaged by STM after deposition onto a Au(111) substrate.[17] All four wheels are visible (Figure 2), but the *p*-carborane wheels appear much

Scheme 2. Synthesis of Nanodragster **1**



smaller than the C_{60} wheels. Due to this difference in contrast between the wheels, on large scale images the molecules seem to have only two wheels unless observed carefully. Figure 2A shows two molecules with two different conformations positioned near step edges. Due to the free rotation

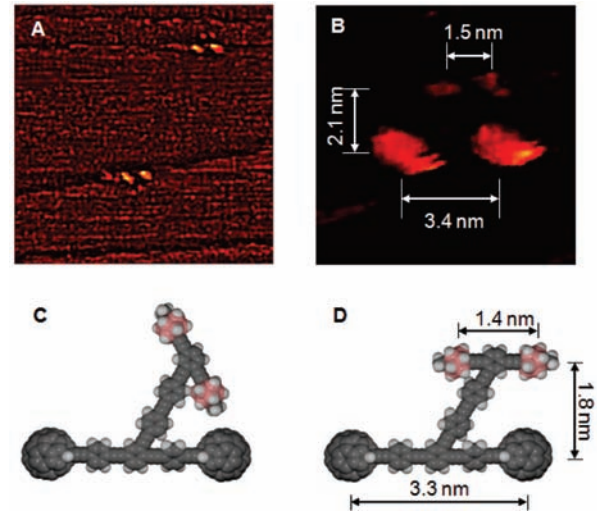


Figure 2. Nanodragsters **1** on a Au(111) substrate at 300 K. (A) A high-pass filtered, large area STM image of two nanodragsters in different orientations near step edges (bias voltage [V_{bias}] = −100 mV, tunneling current [I_t] = 0.2 nA, image size: 63.8 × 63.8 nm^2). (B) A high-resolution STM image of the nanodragster indicating the associate wheel spacings (V_{bias} = −75 mV, I_t = 0.25 nA). (C−D) Models of two conformations of **1** as they are seen in image (A). Also shown are the calculated distances that correlate with measured dimensions in (B).

(17) Sample Preparation and Data Collection for the STM Study: A toluene solution of **1** (5 μM) was dosed with two 25 ms pulses into high vacuum using a fast-actuating, small orifice solenoid valve[18] onto argon-sputtered and annealed Au(111) on mica substrates and was imaged using an Omicron UHV STM controlled by RHK electronics. The dosing technique was chosen over sublimation in vacuum, as it appeared in thermal decomposition studies using a thermogravimetric analyzer in our previous work that C_{60} nanocars were thermally sensitive.

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along the triple bonds, **1** has multiple conformations accessible when adsorbed on the surface, and examples of two such structures are shown (Figure 2C and D). If the two axles are parallel, linear motion is expected, whereas if they are angled, circular motion should be expected. The *p*-carborane wheels are clearly visible in the subsequent zoomed-in image (Figure 2B). The dimensions of the molecule in the STM image are in good agreement with the one obtained after geometry optimization with MS modeling.[19]

In summary, we have synthesized a mixed wheeled nanovehicle composed of a *p*-carborane-wheeled front axle and a C_{60}-wheeled rear axle; this arrangement is called a nanodragster. Initial STM imaging shows the two type of wheels and should help to establish the role of *p*-carborane wheels in directional rolling motion. Variable-temperature STM measurements are currently underway to compare the motion of these molecules with that of the all C_{60}-wheeled nanocars.

(19) Geometry optimized by molecular mechanics with universal force field and forcite package, Materials Studio (MS) Modeling 4.0.

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Supporting Information Available: Synthetic procedures, ^{1}H NMR, ^{13}C NMR, and IR of compounds **1**, **4**−**6**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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