

From fullerene- C_{60} to four-wheelers

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Buckminsterfullerene (C_{60}), the third form of carbon, was first reported from Rice University, Houston in 1985 by Smalley and co-workers¹. C_{60} has several unique distinctions – it is the only allotrope of an element to be discovered in the twentieth century and has the maximum number of atoms in a molecule of an element. Further, the structure of this form of carbon is perfectly symmetric and hence a soccer ball-like structure has been proposed by the inventors. Several amazing discoveries followed soon after the announcement of the large-scale preparation of C_{60} by electric arc discharge method². It is the invention of fullerene that is responsible for the discovery of carbon nanotubes (CNTs). A careful examination of the carbon cathode used in the arc discharge process for preparing small carbon clusters by Sumio Iijima³ in 1991 resulted in the remarkable discovery of CNTs, and that is indeed a milestone in the study of different forms of carbon.

The impact of the prophetic and famous address entitled 'There is plenty of room at the bottom' to the Meeting of the American Society of Physics in 1959 by Richard P. Feynman, is so enormous that miniaturization is no longer a matter of scaling down a macroscopic counterpart. Since then, for preparation of a nanostructure, bottom-up approach is being attempted and it involves collection, consolidation and fashioning individual atoms and molecules into the structure. In spite of tough challenges on the construction and control, nanolevel machines, i.e. molecular-level machines akin to macroscopic motors, switches, shuttles, gears and elevators are now known^{4,5}.

At Rice University, enough C_{60} was available for other scientists and engineers to play with the bucky ball. It is no wonder they thought that because of its spherical shape, C_{60} might be employed as wheels in a molecular transporter. A car is a device on wheels for transporting people or objects. A big or a small car, a transporter, usually contains a chassis, axles and four wheels to roll. A nanometre-sized vehicle will be a suitable transporter in future for drug delivery at the appropriate place and for other purposes. It was a challenging task to attach axles

and chassis made of well-defined organic groups with pivoting suspension to fullerene wheels. Tour's research group at Houston spent almost eight years to complete the construction of nanocars. Last year, this group⁶ reported nanocar-1 (Figure 1). A space-filling model of nanocar-1 is shown in Figure 2.

While four fullerene molecules constitute the wheels of a nanocar, axles and chassis are made of well-defined organic groups with pivoting suspension and freely rotating axis (alkynyl groups and oligophenylene ethynylene groups) and details of the synthesis have been recently reported⁷. Synthesis and testing of nanocars and other molecular machines is providing critical insight to bottom-up molecular manufacturing. The entire car measures just 3–4 nm across, making it slightly wider than a strand of DNA. A

human hair, by comparison, is about 80,000 nm in diameter.

Though proving that the nanocar is rolling on the surface and not slipping and sliding is a rather difficult job, scanning tunneling microscopy (STM) measurements and experimental evidence confirmed the rolling movement.

The nanocar needs a special surface to move. It was found that movement of nanocars across a gold surface is possible. STM imaging studies demonstrated that nanocars were stable and stationary on gold surface at room temperature for a wide range of tunnelling parameters (Figure 3). This stability is attributed to a relatively strong adhesion force between the fullerene wheels and the underlying gold. Earlier, this type of bonding for fullerenes on metals had been observed⁸. The nanocar is rectangular (not square)

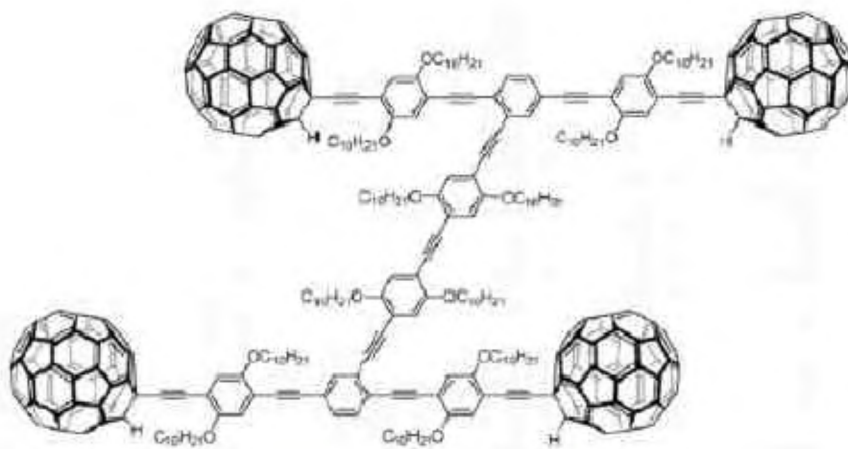


Figure 1. Fullerene-wheeled nanocar-1. Reprinted in part with permission from Shirai *et al.*⁶. Copyright (2005) from American Chemical Society.

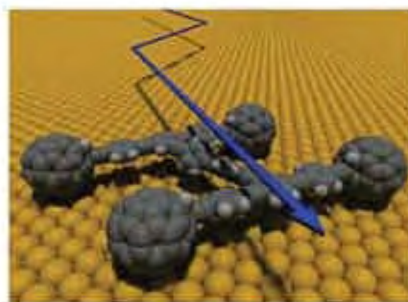


Figure 2. Space-filling model of nanocar-1. Reprinted in part with permission from Shirai *et al.*⁶. Copyright (2005) from American Chemical Society.

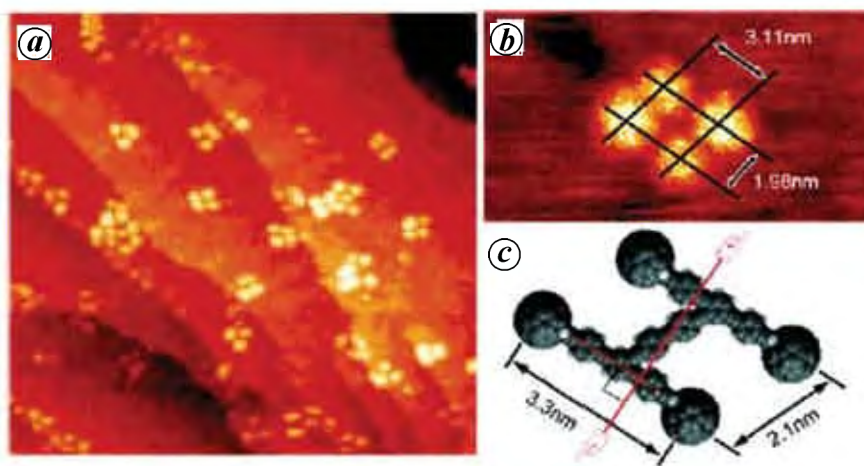


Figure 3. Nanocar-1 on Au(111) surface: (a) STM image of nanocar-1 deposited on Au(111). Bright features are fullerene wheels and the organic groups are not visible. (b) High-resolution STM image. Orientation of the molecules can be determined by fullerene peak-to-peak distances, with (c) modelled distances at 3.3 nm across the width and 2.1 nm across the length, or the axle and chassis direction respectively, as shown in the alkyl-free space-filling model. Red fingers indicate the expected direction of rolling perpendicular to the axles. Reprinted with permission from Shirai *et al.*⁶. Copyright (2005) from American Chemical Society

as its axle is slightly longer than the wheelbase – the distance between axles (Figure 3). Therefore, using STM imaging it is possible to know the way the car is oriented. It has been found that nanocar-1 moved perpendicular to the axles.

The motion of the car is thermally induced and has been followed by STM imaging. When the temperature of the surface was raised up to about 170°C, the nanocars remained almost stationary and beyond this point, the molecules started to move in two dimensions through a combination of both translation and pivoting, and not in the 1D manner initially anticipated. Around 200°C, the motion of the nanocars is slow enough that it could be followed through a sequence of images. (Two STM movies are available at the website: <http://tourserver.rice.edu/movies/>). Despite the fact that the observed motion is in 2D, imaging studies demonstrate that the translational movement of the nanocar-1 occurs in the direction perpendicular to its axles. It was not possible to track the movement beyond 225°C because of the rapid and erratic motion of the molecules. The movement of nanocar-1 could also be electrically induced (STM-tip field). The sequence of manipulation studies with STM tip demonstrates a strong directional preference favouring motion perpendicular to the axles.

Tour and coworkers⁹ also started designing different types of nanocars. They have reported the synthesis of a nanocar-2 that bears a light-powered molecular motor in its central portion for the ultimate paddlewheel-like propulsion action along a substrate surface for motion of nanocar-2 as depicted in Figure 4. Perceptible differences between nanocars 1 and 2 may be noticed in the wheels and chassis. In the second car *p*-coronanes⁹ are preferred as wheels and Feringa's motor¹⁰ (sulphur containing group) is used in the construction of chassis for light absorption.

Though kinetic studies in solution show that the motor indeed rotates upon irradiation with 365 nm light, STM image studies have not been reported.

A truck is usually a vehicle for handling loads. Shirai *et al.*⁷ constructed a nano-sized device on wheels that has a platform which might accommodate a load, and they christened this as a nanotruck. Nanotruck-1 (Figure 5) has a potential loading bay (acid–base bonding to the nitrogen atoms), unlike nanocars-1 and 2. Another

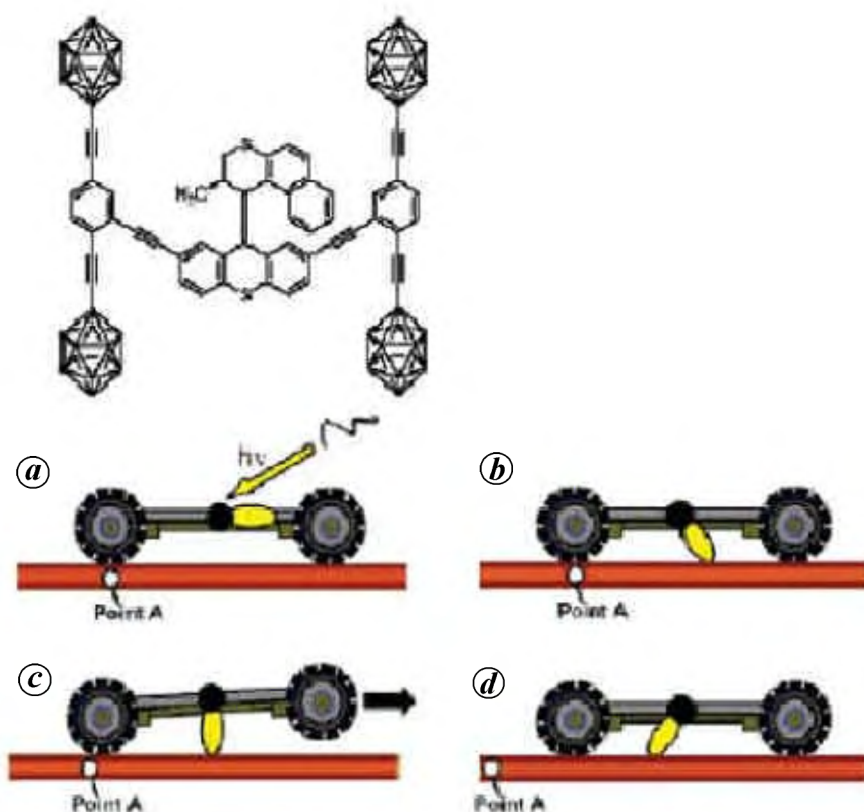


Figure 4. (Top) Structure of motorized nanocar-2. Colour figures: Proposed propulsion scheme for motorized nanocar-2 where (a) 365 nm light would impinge upon the motor which in conjunction with a heated substrate (at least 65°C), (b) affording motor rotation and (c) sweeping across the surface to (d) propel the nanocar forward. Reprinted with permission from Morin *et al.*⁹. Copyright (2006) from American Chemical Society.

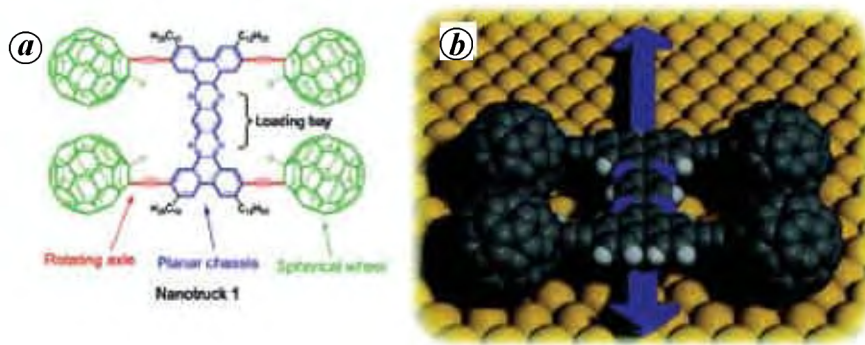


Figure 5. (a) Molecular structure of fullerene-wheeled nanotruck-1 and (b) space-filling model of nanotruck-1 (devoid of dodecyl groups for clarity). Reprinted in part with permission from Shirai *et al.*⁷. Copyright (2006) from American Chemical Society.

nanotruck was also synthesized and the difference between nanotrucks 1 and 2 lies only in the organic components in the axles. However, detailed STM imaging on the two trucks was hampered due to contamination of gold surfaces with unreacted fullerenes and possible instability of the nanotruck structure on surfaces.

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