Molecule Concept Nanocars: Chassis, Wheels, and Motors?

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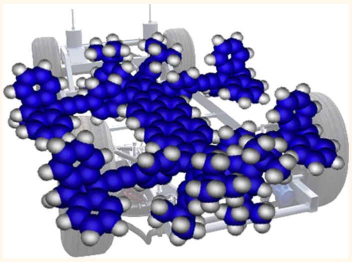
ABSTRACT The design, synthesis, and running of a molecular nanovehicle on a surface assisted by proper nanocommunication channels for feeding and guiding the vehicle now constitute an active field of research and are no longer a nano-joke. In this Perspective, we describe how this field began, its growth, and problems to be solved. Better molecular wheels, a molecular motor with its own gears assembling for torque transmission must be mounted on (*i.e.*, chemically bonded to) a good molecular chassis for the resulting covalently constructed molecular nanovehicle to run on a surface in a controlled manner at the atomic scale. We propose a yearly molecule concept nanocar contest to boost molecular nanovehicle research.



For building complex machines, mechanical properties were used long before the electronic properties of materials. The Anticythere clock[1] was constructed centuries before the discovery of the electronic rectification effect by Braun in 1874. Both were at the origin of the construction of true mechanical and electronic calculators, respectively. Interestingly, for nanoscale machines, electronics started to be envisaged before the mechanics, realized with the seminal molecular rectifier paper written by Aviram and Ratner in 1974.[2] At the beginning of the 1970s, a challenge was put forward by the Pasteurian Jacques Monod urging physicists to create better devices that could compare to a single protein in processing a signal.[3] Today, transistors are nanofabricated in nanoelectronics laboratories with a source–drain distance below 10 nm, the size of a protein. After its initial start at the end of the 1990s,[4] single-molecule mechanics now shows up progressively. This was certainly boosted by the invention of the scanning tunneling microscope (STM) and the discovery that a large molecule can be manipulated with a precision better than 0.1 nm.[4]

In molecular electronics, the shape of the single molecule involved, for example, in a rectification effect when jumping over a metal–insulator–metal planar tunnel junction, does not tell much about the molecule functionality. To produce the rectification effect in this junction, the intramolecular quantum physics in action is independent of the overall shape of the molecule. For single-molecule mechanics, there is still good correspondence between the molecule's chemical structure and its functionnality. When adsorbed on the supporting surface where it functions, the mechanics of the molecule machine is almost classical. The quantum decoherence of the mechanical part of the molecular wave function on the surface renders the soft mechanical mode of this molecule almost classical. Therefore, molecule wheels, gears, motors, clips, and vehicles generally take the shape of their macroscopic or their intermediate protein scale equivalents. The new molecule nanocar presented by the Tour group in this issue of *ACS Nano* follows this trend.[5]

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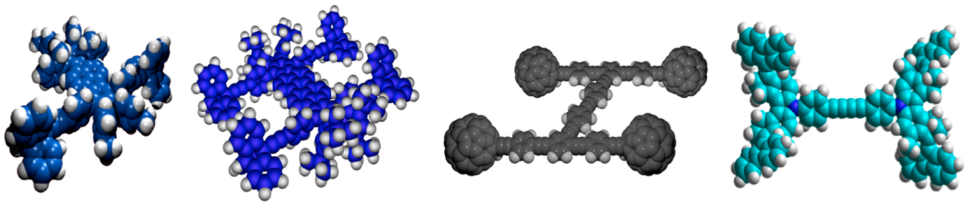

Figure 1. Examples of molecular nanovehicles. From left to right, the original molecular wheelbarrow, a nanovehicle with triptycene wheels, a nanovehicle with C_{60} wheels and with four switchable legs instead of wheels.

Interestingly, the first design and synthesis of a molecule-wheeled nanovehicule was the end result of a joke. During a discussion about the use of the lander molecule concept (a molecule equipped with four legs, used for studying single-molecule electronic contact to a metallic step edge), a physicist colleague of ours passed by the meeting room. As the researchers were joking about different possible switchable legs, our dear physicist challenged us to consider substituting wheels instead of legs to create a molecular wheelbarrow. Soon after, the corresponding molecule was designed[6] and synthesized.[7] Then Tour and collaborators proposed and synthesized the first three- and four-wheel molecular nanovehicles.[8,9] The new contribution of the Tour group in this issue of *ACS Nano*[5] is the result of intense efforts by his group at Rice University to deliver better nanovehicles and to approach the grand challenge of synthesizing a single covalent molecule that contains in its chemical structure a chassis, a certain number of wheels (or switchable legs), and, maybe one day, a motor chemical group to power the displacement of the molecular vehicle along its supporting surface.

How nanovehicle chassis and wheels interact with a surface is being actively explored. For the chassis, two strategies have emerged. As presented in Figure 1, one can use a polyaromatic hydrocarbon that combines the rigidity of those types of molecules with space for a cargo zone to be able to carry an atomic-scale load.[10] But for chemists, this usually leads to a solubility problem during synthesis, unless the synthesis is performed directly on the supporting surface. Other researchers, like the Tour group, have preferred to work with a flexible chassis where there is still full control over the distance and position of the wheels along the chassis but with more degrees of freedom leading to more soluble families of molecules.[8]

Triptycene chemical groups were the first wheels mounted on a molecular chassis. Linked to an axle, the rotation of double-wheel axle machinery was studied using the tip apex of an ultrahigh vacuum low-temperature (LT-UHV) STM to push on one of the two wheels. The wheel rotation was followed by recording the real-time STM tunneling signal while performing single-molecule manipulation.[11] The synthesis of four-wheeled nanovehicles equipped with triptycene wheels did not turn to a movable molecule because the triptycenes tend to adsorb strongly on the supporting metal surface by parallelization of their two phenyl rings relative to the surface.[12] Many different kinds of molecular wheels have now been synthesized, as presented in Figure 2. The Tour group has been active in this research, proposing for example [60]-fullerene[8] or *p*-carborane wheels.[13,14] The adamantane wheels equipping their new nanocar, which is presented in this issue of *ACS Nano*,[5] are an attempt to get more mobile nanocar molecules on a surface. We have also synthesized new competitive molecular wheels, like the subphthalocyanine wheels, in an effort to combine the strong rigidity of their backbone with low surface

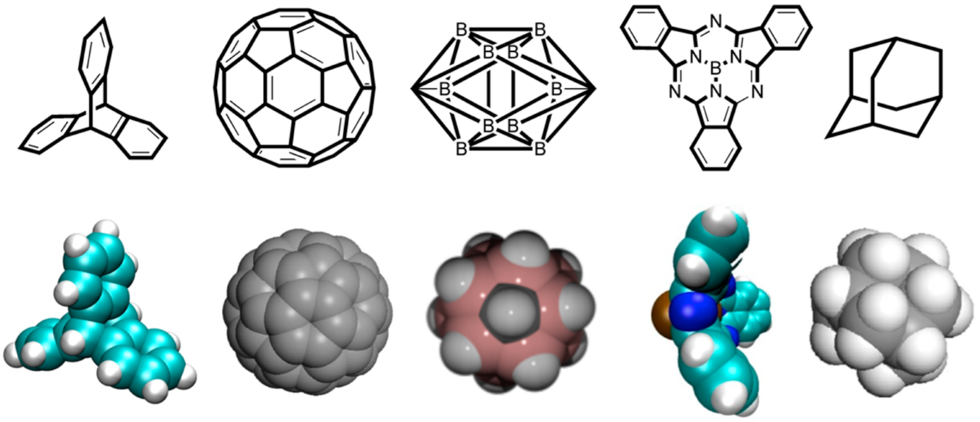

Figure 2. Molecular wheels already used to build molecular nanovehicles. From left to right: triptycene, [60]-fullerene, *p*-carborane, subphthalocyanine, and adamantane. The chemical structures are shown above and CPK 3D model below.

interactions thanks to their bowl-shaped structures. The orthogonal bonding to the nanocar axle renders it impossible to have them parallel to the surface.[15,16] Tagging the wheel to follow their step-by-step rotation in the time-dependent tunneling current signal of an LT-UHV-STM was a nice innovation coming from the study of molecular gears, another branch of single-molecule mechanics.[17] This tagging will soon be adopted by other molecular nanocar designers to facilitate the certification of wheel rotation on the supporting surface instead of wheel diffusion. The presented adamantane-wheeled nanocar has also been equipped with an emitting chemical group,[14] which allows the researchers to follow the displacement of the nanocar along the surface using fluorescence optical microscopy instead of a LT-UHV-STM. This is another innovation for molecular nanocars, which will also likely be adopted by other nanocar designers.

Often after describing molecular nanovehicle research to the public, the same question arises from the audience: "Very nice indeed, your concept car, but where is the motor?" Of course, there is not a lot of space on a few-nanometers-long molecular chassis to mount a motor covalently that is a chemical group able to transform the provided energy for motion into a true motive power. In a previous study, the Tour group proposed chemical propulsion from a chemical reaction.[18] The major drawback of this strategy is the generation of molecular waste on the surface. To lower the diffusion barrier height for their molecular nanocar on metallic surfaces, the Ferringa group have controlled the conformations of the four legs, driving their nanocar with inelastic tunneling electrons.[19] However, by suppressing the need for a permanent physical link to the molecule and without producing chemical waste, light access seems to offer an ideal nanocommunication channel for sourcing the motion; some examples have been described.[13,19] Nevertheless, for the energy source of propulsion, one can envisage using tunneling electrons provided by the tip of a STM to create step-by-step clockwise or counterclockwise rotation of a molecular wheel mounted on a single atom axle, as was recently demonstrated.[20,21] This, however, requires designing much larger covalent molecular architectures to be able to mount such a molecular motor on the nanocar chassis and to direct the torque produced to the wheels. No such motorized molecules have yet been designed. However, with the purpose, for example, of driving the rotation of a solid-state nanogear, the synthesis and control of molecular motors attached to an ultraclean surface are becoming an active field of single-molecule mechanics research.[20−25]

To speed up the synthesis of motorized nanovehicles, let us propose a yearly competition whereby all nanocar designers would meet together for a few days, similar to the microrobotics contests held around the world. In the 1970s, the Monod challenge was for electronics and to defend the computing power of macromolecules against electrical relays. Today, molecular nanocar designers will bring their molecule as a powder or liquid to the nanorobotic contest to defend their motorized molecule nanocar proposal. A LT-UHV-STM or a LT-UHV noncontact atomic force microscope (NC-AFM) will be provided to challenge each other under the microscope. Of course, the competition will have to be prepared in advance to equip the microscope with the nanocommunication channels required to drive their molecular nanovehicles in competition. We now have to decide the rules of the competition and what will be the award—perhaps a nice macroscopic racing car?

Conflict of Interest: The authors declare no competing financial interest.

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