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Electric Nanocar Equipped with Four-Wheel Drive Gets Taken for its First Spin

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Nature provides many wonderful examples of molecular machines including motor proteins that perform a variety of tasks like chromosome segregation, cellular trafficking, and locomotion. By contrast our current technology, with the exception of liquid crystals, is still far from utilizing the nanoscale motion of molecules. This gap stems in part from a lack of understanding of how energy flows into and through molecular degrees of freedom in all but the simplest of systems. Over the last decade synthetic molecular machines powered by light, chemical and electrochemical reactions have provided proof of principle for such devices, but electrical control over molecular motion has remained more elusive.[1] The flow of energy from electrons to electronically or vibrationally excited states is very complex and difficult to model theoretically in larger molecules. This is especially true for molecules on surfaces which are the most amenable to electrical excitation from scanning probe tips. Therefore, the challenge is to design systems that are complex enough to exhibit the desired behavior, yet simple enough to be synthesized and have the rate and directionality of their motion quantified.

Hot on the heels of our discovery of a single-molecule electric motor,[2] groups lead by Feringa and Ernst have just reported a nanocar comprised of a single molecule that is capable of unidirectional motion over a metal surface powered by electrons from the tip of a scanning tunneling microscope (STM).[3] The first nanocar was built in 2005 by the Tour group and driven by a team headed by Kelly.[4] The molecules were composed of a similar chassis to Feringa's car but had symmetric C_{60} wheels. Even though their thermally driven motion was two-dimensional, the translational movement of the nanocars occurred in the direction perpendicular to their axles,[4] illustrating the opportunity to direct molecular motion on surfaces with chemical structure.[5] However, in terms of biasing forward over backward motion, as thermodynamics dictates, one cannot get useful work from a system at thermal equilibrium.[6]

Feringa and Ernst's approach used the tunneling current from an STM tip as a source of energy so their nanocar would not be subject to this thermodynamic constraint. They carefully constructed the nanocar with four wheels that had different chirality on opposite sides of the molecule. This provided the necessary asymmetry and yielded motion only in the forward direction. It is important to note both the enormous challenge in making the nanocar in its correct chiral arrangement and then being able to deposit it cleanly on a surface without decomposition. An elegant synthesis coupled with careful STM measurements enabled Ernst and Feringa to demonstrate a set of molecules that exhibited either linear or random motion, depending on the chirality of each of their individual motorized wheels.

Figure 1 shows the detailed chemical structure of the nanocar and illustrates how electrical excitation of the motion occurs by placing the STM tip above the molecule and tunneling into it at elevated bias. Ernst's group used voltage-dependent experiments in which tunneling electrons of different energies were used to excite the molecule, while its motion was measured by STM imaging before and after excitation. These studies revealed that the motors inched forward through a sequence of lower energy (ca. 20 kJ mol^{-1}) helix inversions driven by vibrational excitation and higher energy (ca. 50 kJ mol^{-1}) C=C isomerizations induced through an electronically excited state of the motor.

Only molecules with the correct chirality of wheels exhibited directional (almost completely straight) motion whereas molecules in which the wheels on opposite sides of the chassis turned in opposite directions resulting in spinning and random motion. These facts supported the authors' conclusion that the highly directional transport was a consequence of the specific molecular design and not an artifact of the measurement process.

Although the temperatures at which the nanocar operates make this type of system far from being useful in practical devices, it is one of a small number of studies that offer insight into how energy is transferred into motion at the single-molecule level. At this point in time the mechanical action of photo-, chemically- and electrochemically-driven systems is somewhat easier to detect and harness. For example Feringa's group have previously embedded their light-driven molecular motors in a liquid crystal film and showed that micrometer-sized glass rods floating on the surface could be controllably rotated.[7] However, as one thinks about longer-term applications, the real advantages of electrically driven synthetic molecular motors will be that one can excite single or small

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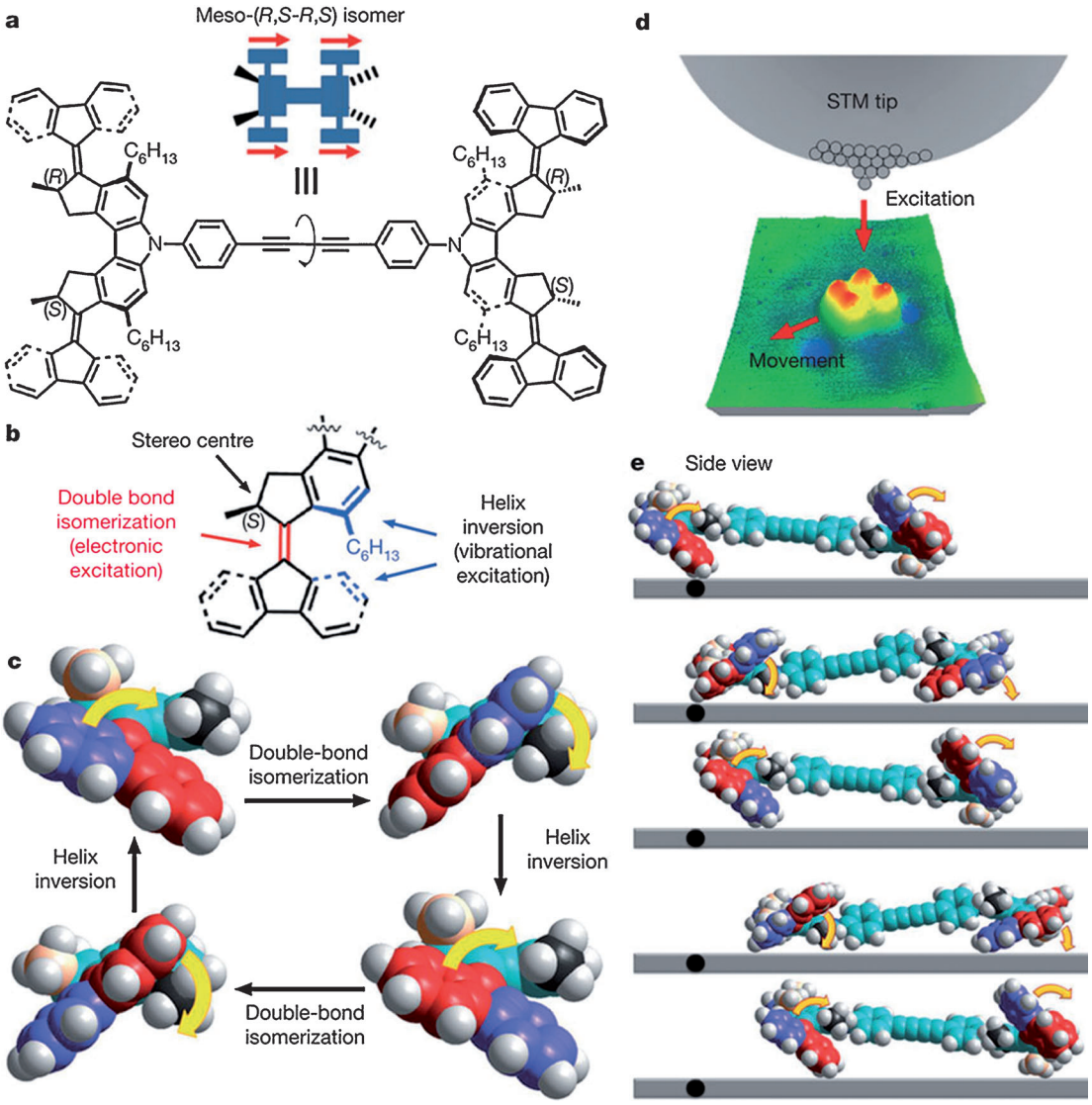

Figure 1. Illustration of the nanocar's structure and dynamics of its motion across the metal surface. a) Chemical structure of the nanocar including the chirality of each of the four wheels. The car's electrically excited trajectory along the surface is indicated by the red arrows. b) Detailed structure of one of the motorized wheels. c) Snapshots of the 360° rotation of the rotary motor which involves two double-bond isomerization and two helix inversion steps. d) Illustration of excitation of the nanocar by electrons from the STM tip. e) Molecular models showing the configuration of the nanocar during different stages of its motion. Adapted by permission from Macmillan Publishers Ltd: Nature,[3] copyright 2011.

groups of molecules with electricity more easily than with either chemical fuel or light. In fact, current commercial lithographic techniques routinely manufacture metallic feature sizes on the tens of nanometers scale, therefore, it is not unreasonable to imagine future opportunities for interfacing individual or small groups of electrically driven molecular motors with Si chip based devices.

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