How to build and race a fast nanocar

Grant J. Simpson, Víctor García-López, Philipp Petermeier, Leonhard Grill and James M. Tour

The first NanoCar Race was an opportunity to see how far we have come in manipulating single molecules. As the team with the fastest molecule in this race, we share the synthetic challenges to building a fast nanocar and the experimental approach needed for rapid translation across a surface.

On 28 and 29 April 2017, six teams raced their nanocar across a predefined track at the Center for Materials Development and Structure Studies (CEMES-CNRS) in Toulouse, France[1]. The goal of the initiative was primarily to foster interdisciplinary collaborations between synthetic chemists and experimental physics. Participants had to (1) design and synthesize a nanocar and (2) drive it on a metal surface at ~5 K with a scanning tunnelling microscope (STM) tip for 100 nm (on gold) or 150 nm (on silver). The propulsion method had to be either the tip-induced electric field gradient or the inelastic electron tunnelling current. No mechanical manipulation, such as pushing with the STM tip, was permitted[2]. The nanocars were deposited on the metallic surface and then located by STM imaging throughout the race.

Our nanocar (Dipolar Racer) completed the race in less than 2 hours, whereas some other cars never crossed the finish line in the allotted 30 hours. So, why do nanocars differ in their ability to translate rapidly on a surface?

We explain here the key features in nanocar design and molecular manipulation (racing) strategies we implemented into the Dipolar Racer. Many of these features were determined empirically to enhance the velocity, manoeuvrability and function of molecular machines[3] through more than a decade of nanocar design and expertise in STM manipulation.

The features needed in a nanocar design to enhance speed are as follows:

(1) Molecular weight: keep it as low as possible. Larger nanocars are harder to deposit intact under ultrahigh vacuum conditions and their added structural moieties provide more sites for surface adhesion, thereby raising the diffusion barrier and consequently slowing the nanocar.

(2) Wheels: keep them aliphatic rather than alkenyl, aromatic or heteroatomic to minimize surface interactions (examples are given in Fig. 1a)[4]. They should be large enough to lift the chassis off the surface to minimize chassis–surface attraction. Note that, in the case of this race, distinguishing between surface sliding and wheel rolling[5] was not a requirement. The Dipolar Racer has adamantane wheels since they are aliphatic while being relatively spherical (Fig. 1b). Moreover, the number of wheels necessary to raise the chassis
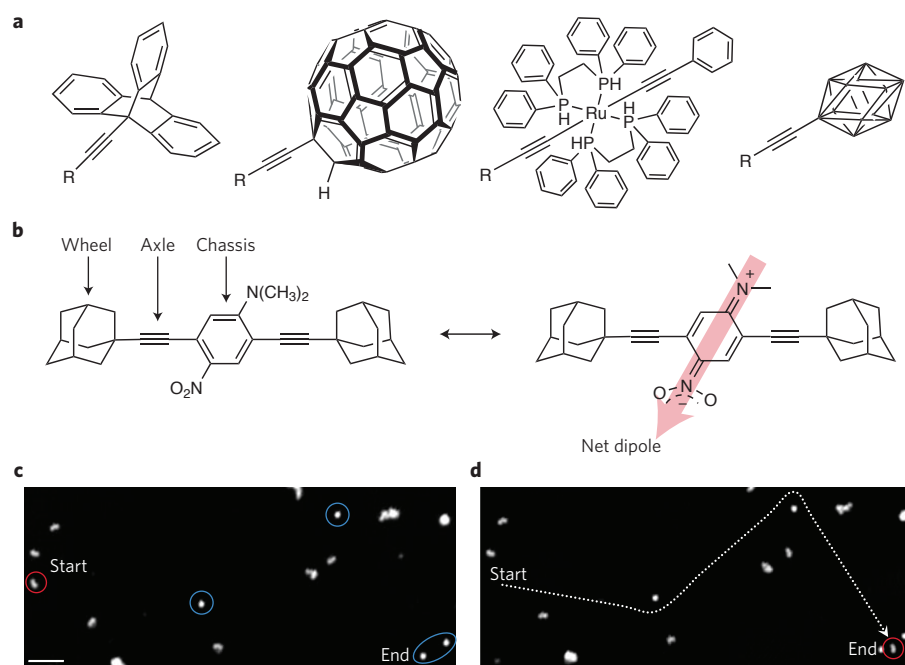

Figure 1 | The Dipolar Racer molecule and the nanocar racetrack. **a**, Four types of wheel–axle combinations that have been tried where the 'R' moiety is the chassis bonding point and the axle is based on an alkyne. These include, from left to right, triptycene, C_{60}, an organometallic complex and *para*-carborane, where each of the vertices is a BH bond except at the alkyne attachment point and the *para*-position being C and CH, respectively. **b**, Molecular structure of the Dipolar Racer and its resonance form, which highlights the strong net dipole in the direction of the dipole arrow. The Dipolar Racer is ~1.6 nm × 0.6 nm. **c**, STM image (120 × 50 nm²) of the Ag(111) surface at the start of the race showing a Dipolar Racer nanocar (red circle) on the left with two nearby nanocars, the two asperity pylons and the finish line between the juxtaposed pylons (blue circles). **d**, STM image of the same surface area at the finish of the race where one Dipolar Racer molecule (red circle) has passed the finish line. The 150 nm racecourse followed is shown with the dotted line. Scale bar, 10 nm.

off the surface needs to be carefully determined. The more wheels, the greater the surface adhesion, the slower the nanocar. The Nanocar Race had no requirement on the number of wheels[2]; three of the teams even used molecules without any wheel-like side group.

(3) Chassis and axles: the chassis should be rigid and the axles as short as possible to prevent the overall structure from sagging towards the surface, thereby minimizing chassis–surface interactions. However, axles have to be long enough to minimize steric interactions between the wheels and chassis, and there must be free rotation about axles to minimize rotational barriers. The Dipolar Racer had mono-alkynes to fulfil this role. Lastly, a strong dipole in the chassis can aid in the STM-induced translation of the nanocar.

(4) Stability: the molecular structure should be sufficiently stable to be deposited under ultrahigh vacuum and to mitigate reduction or bond breakage that could destroy the molecule under STM-tip voltage pulsing.

After the molecule is synthesized, purified and spectroscopically characterized to confirm its structure[6], racing considerations come into play. The nanocar should be as fast as possible, challenging the STM measurements in terms of manipulation, that is, stimulation of the molecule in the most efficient way to quickly arrive at the finish line (Fig. 1c,d), and also in terms of imaging, that is, identification of the molecular location during the race. It is worth noting that our nanocar moved uncontrollably fast on a gold surface even during STM imaging, so we selected to race on silver.

A large number of studies have shown that atoms and molecules can be displaced laterally in a controlled way on a supporting surface[5,7,8]. While various interatomic forces can cause translation, 'pushing' with the STM tip is often the preferred mechanism in the case of molecules[9], as relatively strong forces — required to overcome the diffusion barrier — can be achieved by Pauli repulsion. However, for the purpose of the nanocar race, such a mechanical pushing mechanism was forbidden[2]. The Dipolar Racer (Fig. 1b) was therefore equipped with a strong net dipole in the chassis[10] so that interaction with the electric field of the STM junction is accentuated. Interestingly, to promote a strong donor–acceptor interaction, the dimethyl groups must become coplanar with the aryl ring, as shown in Fig. 1b (right resonance form).

To cause lateral translation of single molecules by electrostatic forces, the STM tip was brought next to the molecule of
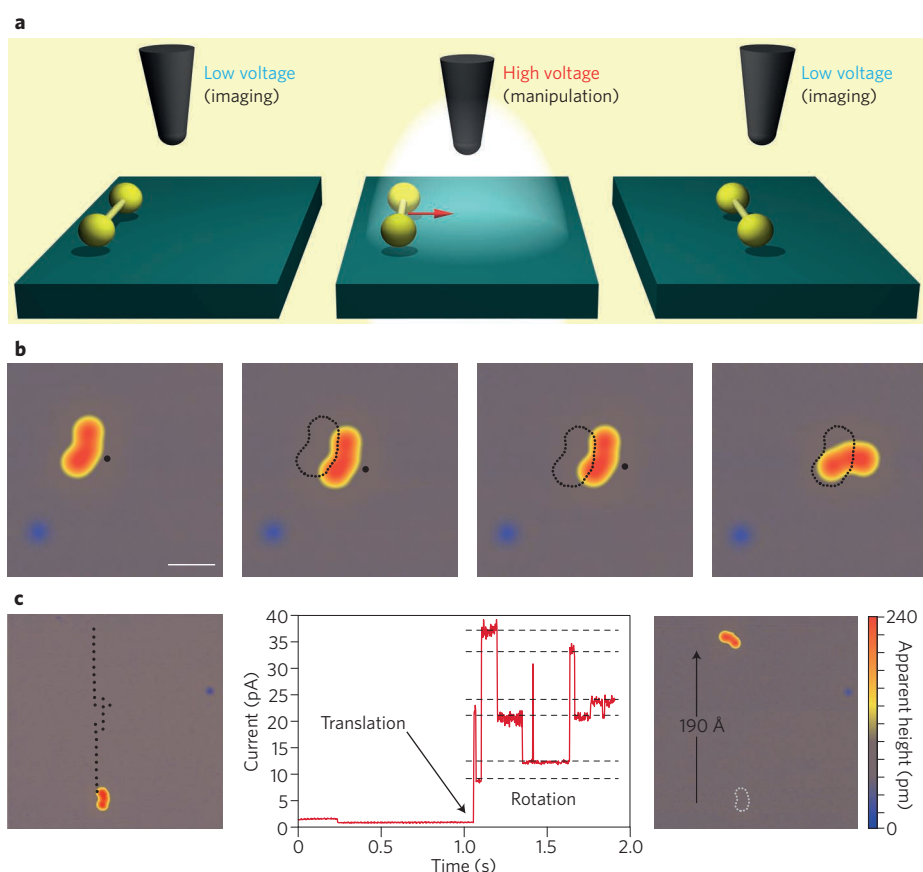

Figure 2 | Single-molecule manipulation by STM. **a**, Schematic of the controlled manipulation procedure. Low voltage (0.70 V) is used for imaging the molecule and high voltage (1.8 V) is used to induce movement. In the manipulation step, the increased electric field strength attracts the dipolar molecule to the region directly below the STM tip. **b**, Series of STM images showing stepwise translation of the molecule, relative to a fixed reference point (surface defect) at the lower left, following successive voltage pulses (induced at indicated black spots) while the original location of the nanocar is highlighted by the black outline. Scale bar, 2 nm. **c**, Fast translation procedure. Left STM image: individual voltage pulses (series of black dots from bottom to top) are performed over a long distance (with respect to a fixed surface defect at the right edge of the image) without imaging between each step. Centre: an order of magnitude jump in the current versus time plot indicates that the molecule has translated, after which the molecule rotates. Right STM image (of the same surface area; see defect at the right): the end location of the nanocar. STM image parameters: 0.70 V; 0.27 pA. The molecules were deposited from a molecular doser (Kentax) onto a cleaned Ag(111) single crystal, held at approximately 25 K, in an ultrahigh vacuum chamber (1×10⁻¹⁰ mbar). The sample was cooled to 7 K before STM imaging.

choice after imaging and a relatively high bias voltage was applied, causing a strong local electric field. If sufficiently strong with respect to the diffusion barrier on the surface, the resulting attraction leads to a lateral displacement of the dipolar molecule towards the STM tip (Fig. 2a). Afterwards, the molecule is reimaged at lower bias to confirm its new position on the surface. An experimental example of this procedure is presented in Fig. 2b where an individual Dipolar Racer molecule, visible as a peanut-shaped double lobe, is moved along the surface, verifying the molecular displacement by STM imaging after each step. However, imaging the molecule between manipulation

steps is the bottleneck that limits the overall speed because a single image typically takes one to five minutes to acquire.

To maximize the speed of the molecules across the surface, it is crucial to minimize the number of images taken along the way. Although at first glance this appears to be a 'blind' process, such a strategy has been used to build nanostructures from single Co atoms on a Cu(111) surface[11], where the manipulation is very reliable and many steps can be performed without interruption by imaging. However, the manipulation of larger molecules in this way is more complicated since they exhibit many degrees of freedom during lateral motion[12] and typically find

various adsorption geometries in the same location of the surface (whereas single atoms have only one), resulting in different diffusion properties. Thus, in the case of the Dipolar Racer, we decided to measure the tunnelling current during the voltage pulses and use it as an indicator for the extent of the molecular motion, rather than perform repeated imaging. The tunnelling current signal recorded during an STM manipulation has been shown to identify hopping distances and to distinguish between pulling, pushing and rolling modes during a lateral motion of the STM tip over a molecule[5,8]. In our case, this strategy turned out also to be just as informative in static mode, that is, with the STM tip in a fixed position.

In such a process, the STM tip is placed close to the molecule and a bias voltage is applied. A tunnelling current profile is acquired during the pulse for a few seconds (Fig. 2c, middle panel). The plot may contain different regions: a flat region corresponds to no molecular motion and a region with abrupt changes in current corresponds to changes in the molecular adsorption geometry, which occur on a timescale too fast to be resolved by the STM (<20 μs). Two types of molecular motion can be identified to cause current jumps: translation towards and rotation under the STM tip (G.J.S., V.G.-L., J.M.T. and L.G., manuscript in preparation). Using this indicator during a manipulation sequence, the molecule in Fig. 2c is moved in a controlled way by a distance of 19 nm (using 27 voltage pulses) on the surface, without any STM imaging in between. Thus, it is possible to identify from the current signal alone that a successful translation of the Dipolar Racer molecule in

the desired direction along the race track has occurred, without taking images after each step — thus saving precious race time.

The Dipolar Racer completed the 150 nm silver-surface course in a record time of 1 hour and 33 minutes, travelling an average speed of almost 100 nm h^{−1}, and at some points reaching speeds as high as 300 nm h^{−1} (Fig. 1c,d). In addition, we drove the molecule for a total distance of 1 μm over the entire 30 h race duration, breaking another record in nanocar distance travelled through STM-induced field-gradient manipulation. For a series of videos showing the Dipolar Racer along the racecourse see www.nanograz.com/nanocar-race-movie (accessed 19 May 2017) and https://youtu.be/3BfFPhQFKLk (accessed 10 June 2017).

Based on the experience gathered with this NanoCar Race, we suggest two improvements to enhance the speed of molecular nanocars. (1) The molecular dipole embedded in the chemical structure could be made stronger, leading to an increased effect in the local electric field of the STM junction. As long as the diffusion properties remain similar by a comparable molecule–surface interaction, this would most likely result in a higher yield in each individual manipulation step and therefore a faster molecule. (2) The speed might be improved by using software routines that autonomously perform multistep manipulations[11].

The NanoCar Race was a wonderful opportunity to showcase the progresses made in single-molecule manipulation on a surface, but we believe that future nanocar races should be made ever more challenging, for instance, by allowing only molecules driven by incorporated motor units[13,14] or requiring

molecules to pick up atoms or other small molecules from a surface and deliver them to predefined points, or even assemble them into pre-defined — and possibly useful — constructs. Could it be that in a few decades, bottom-up construction using nanomachines will be possible? The NanoCar Race is then a primer for this greater vision. ❐

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References
1. Rapenne, G. & Joachim, C. The first nanocar race, *Nat. Rev. Mater.* **2,** 17040 (2017).
2. *Rules of the Nanocar Race* www.nanograz.com/nanocar-race-rules (CEMES-CNRS, accessed 19 May 2017).
3. Kassem, S. *et al. Chem. Soc. Rev.* **46,** 2592–2621 (2017).
4. Chu, P.-L. *et al. ACS Nano* **7,** 35–41 (2013).
5. Grill, L. *et al. Nat. Nanotech.* **2,** 95–98 (2007).
6. Simpson, G., Garcia-Lopez, V., Petemeier, P., Grill, L. & Tour, J. M. *How to Build and Race a Fast Nanocar: Synthesis Information* http://tournas.rice.edu/website/documents/Experimental_Synthesis_Dipolar_Racer.pdf (accessed 10 June 2017).
7. Eigler, D. M. & Schweizer, E. K. *Nature* **344,** 524–526 (1990).
8. Bartels, L., Meyer, G. & Rieder, K.-H. *Phys. Rev. Lett.* **79,** 697–700 (1997).
9. Moresco, F. *Phys. Rep.* **399,** 175–225 (2004).
10. Sasaki, T. & Tour, J. M. *Tetrahedron Lett.* **48,** 5821–5824 (2007).
11. Celotta, R. J. *et al. Rev. Sci. Instrum.* **85,** 121301 (2014).
12. Alemani, M. *et al. Chem. Phys. Lett.* **402,** 180–185 (2005).
13. Saywell, A. *et al. ACS Nano* **10,** 10945–10952 (2016).
14. Kudernac, T. *et al. Nature* **479,** 208–211 (2011).

The sounds of nanotechnology

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Public perceptions of nanotechnology are shaped by sound in surprising ways. Our analysis of the audiovisual techniques employed by nanotechnology stakeholders shows that well-chosen sounds can help to win public trust, create value and convey the weird reality of objects on the nanoscale.

Most research centres and other stakeholders in nanotechnology produce informational videos about their work to help the public understand what they do. Along with documentaries about nanotechnology, these are the main sources of images that people have of

what science is capable of on the scale of a billionth of a metre.

But these videos have soundtracks too, and it is worth listening to them carefully. We conducted a survey of 108 videos and other audiovisual experiences from 21 countries in the areas of education,

advertising, television, film and art (see Supplementary Table 1). We noted their salient aural characteristics, such as music, tone, voiceover and materializing sound indicators, so that we could identify precisely what aspects of nanosoundscapes are important for achieving key aims