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REPORT ON THE 1ST MOLECULE-CAR RACE

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1. INTRODUCTION

In early 2013, P2.1 Toulouse proposed to organize the first Nanocar Race, i.e. a race involving several molecule 'vehicles' about 1 nm in lateral size. They should be individually driven at the same time and on the same surface by different 'pilots' using a multiple tip scanning tunnelling microscope (STM) [1]. With this announcement, P2.1 Toulouse put forward the challenge of designing and synthesizing robust single molecule-machines that can be controlled individually on a surface. At that time (and still now for the next Nanocar Race II in 2021), the goal was to boost the developments in STM technology, in atomic scale surface preparation and in UHV sublimation techniques of single molecules. In the future, those technologies will make possible the individual control of a single molecule, able, for example, to move on a surface carrying a load, to perform a mechanical work or to carry out a complex Boolean calculation by itself. After almost 25 years of STM experiments testing the mechanical and electronic properties of single molecules, an important goal of the race was also to present to a wide audience the efforts done in STM labs around the world for realizing working machineries with a minimum number of atoms. It was also important to give to a large public a vision of the possibility to build and/or deconstruct nanomaterials and miniature machines atom by atom.

With about 100 atoms and a lateral size of about 1 nm, a molecular nanocar must have a chassis equipped with some spacer chemical groups to hold it a few angstroms away from the supporting surface [1] and an on-board 'motor' [2] i.e. a chemical molecular group allowing the nanocar to move, for example, when tunnelling electrons are flowing through it from the STM tip to the supporting surface. The propulsion mechanism that makes a molecule move on the surface can be either inelastic (that is, related to the excitation of vibrational modes [3] or to current-induced structural changes [4]) or dipolar, resulting from the repulsion/attraction between the nanocar and the bias voltage applied between the STM tip and the supporting surface. Since the nanocar race announcement, it was decided that moving a molecule-vehicle using the well-known pushing, pulling or sliding STM manipulation modes should be forbidden during the race. For the first Nanocar Race edition, the number of atoms per nanocar and the propulsion mechanisms were rather flexible. In a similar way, in the first ever automobile race, held in July 1894 between Paris and Rouen, the weight and engines of the automobiles were quite diverse, while pulling the vehicle with horses or pushing it by human forces was forbidden.

2. NANOCAR RACE I

The nanocar race was hosted in Toulouse with six teams coming from all over the world on the starting line. They were selected among the nine teams that had applied to participate after the early announcement in 2013. The pre-selection of the teams started in 2014 by asking for a detail molecular model, a high resolution LT-UHV-STM image of the molecule-vehicle, and a proof that the molecule can be at least manipulated on a metallic surface with an atomic scale precision. After a few training sessions for each team on the brand new (and unique at that time) LT-UHV 4-STM (Figure 1) installed in P2.1 Toulouse in October 2014 [5], P2.1 Toulouse selected the following six teams among the nine: Basel, Rice–Graz (Graz is the actual P4 MEMO partner), Dresden (The actual P1 MEMO partner), Tsukuba, Toulouse (The actual P2.1 MEMO partner) and Ohio. Training sessions were organized to optimize the molecular sublimation of each type of molecule, especially challenging because the molecular weight of the registered molecules were very different. The sublimation required therefore specific evaporation procedures in UHV, ranging from room temperature diffusion valve to fast pulse evaporation mode. It was also necessary for each team to learn the molecular manipulation software of the P2.1 Toulouse LT-UHV 4-STM.

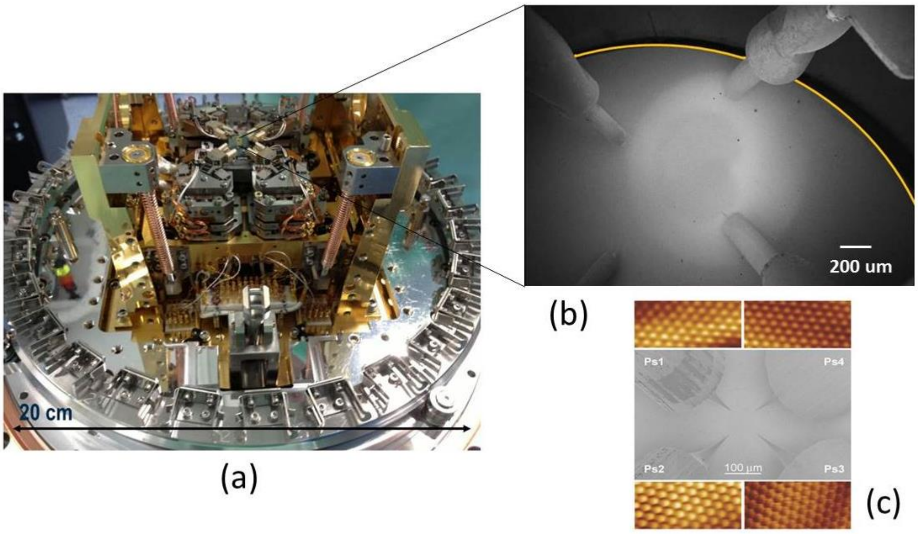


Figure 1: *The LT-UHV 4-STM head constructed by ScientaOmicron for P2.1 Toulouse and used for Nanocar race I. (a) A detail view of the 4 piezo scanners after opening the UHV chamber. (b) An UHV-SEM top view of the four STM tips approaching the Au(111) surface. (c) After approaching the 4 STM tip down to an inter-tip apex distance of about 100 um, the atomic scale images in orange of the Au(111) surface portion scanned at the same time by each tip. Gold atoms are easily imaged with a noise level of about 2 pm at LT (see ref. 5 for more details).*

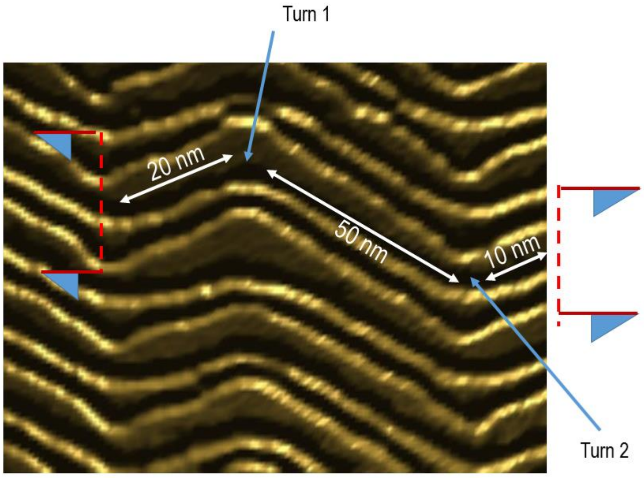


Figure 2: *The race track used during Nanocar Race I by the 5 teams running on Au(111). On this LT-UHV STM image recorded before the race, the surface distance between each track is about 5 nm. The starting and the the arrival line are indicated and where atomic scale marked before the race by each team and certify by the race commissioner. The 2 turns along a track were very difficult to negociate. During the training, it was estimated that the best molecule-vehicle would need at least 30 h to be driven along this about 100 nm drive. It took the Basel team 6.5 h to perform.*

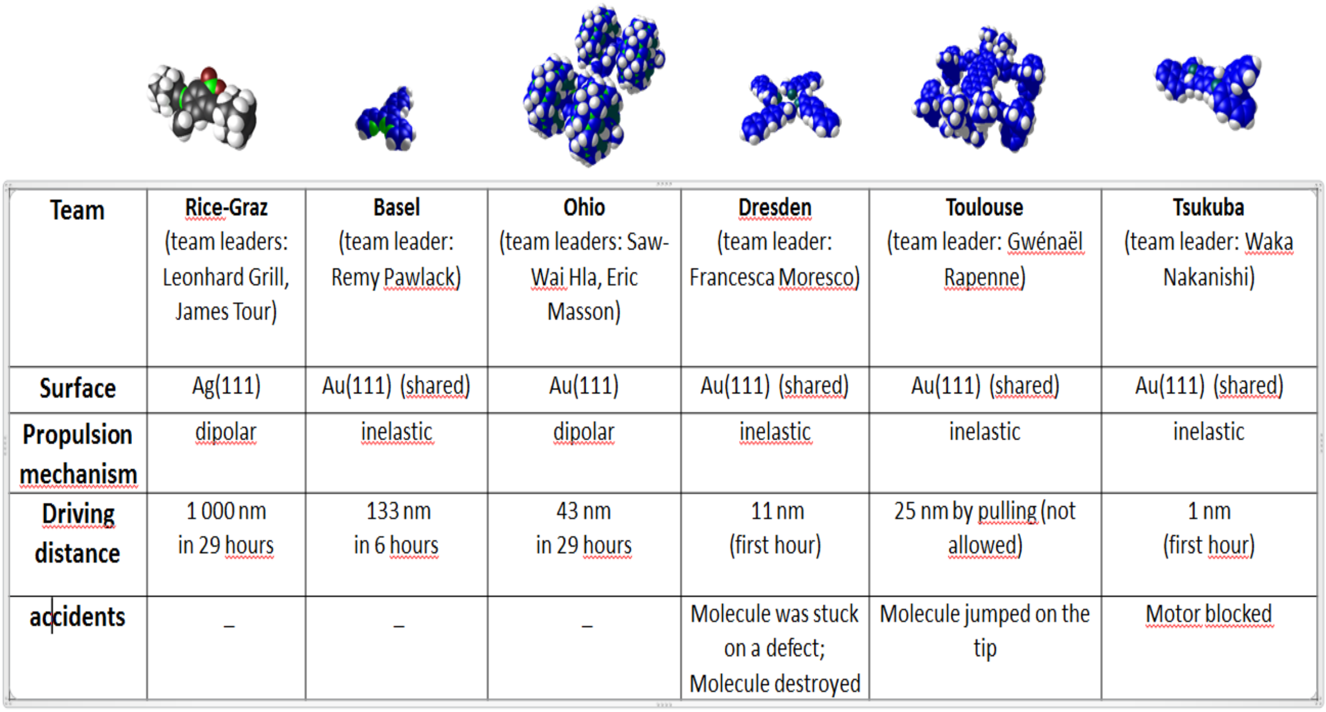
Among the six teams, four drove their nanocars with the new four-tip STM microscope of Figure 1 on the shared Au(111) surface. The two other teams used their own LT-UHV-STM laboratory by remote control. In all cases, the metal surfaces hosting the race tracks were held in ultrahigh vacuum and at a temperature of 4 K. Please note that the remote control of STM single molecule manipulations through the public network across the Atlantic Ocean was already a challenge. Each track for the race was 100 nm long and contained at least two turns (Figure 2). One team raced on an Ag(111) surface, all others on an Au(111) surface.

At exactly 11:00 am on the 28th of April 2017, the departure flag was raised in the P2.1 Toulouse control room (See Figure 3). At 5:00 pm of the following day and after two days and one night of intense effort, the first ever international Nanocar Race was over. It was broadcasted live with the possibility for the general public to have their questions answered in real time. It was a success, both in terms of outreach and of gained scientific insight.

Figure 3: *The first Nanocar Race control room with all the six teams active (from left to right: The Ohio, the Basel, the Tsukuba, the Rice-Graz, the Dresden and the Toulouse teams). This photo was taken at 22:00 pm on the 28th of April 2017. Each team had at its disposabl 2 control screens connected to the control computer and one portable PC for recording its LT-UHV STM image and trace its molecule-vehicle trajectory.*

3. THE FINAL RANKING

Two teams were ranked equally at the first position: Rice–Graz and Basel. The Rice–Graz team successfully completed a very long 1 µm drive in exactly 29 hours on a Ag(111) surface [6]. The Basel team had driven its nanocar for 133 nm on the shared Au(111) surface, crossing the finish line in 6.5 hours [7,8]. The Ohio team was declared third with a 43 nm active drive during 36 h. Their nanocar, composed of about 650 atoms, was the largest participating to the competition. The Dresden team was declared fourth with 11 nm drive [9] and win the perseverance prize. Their nanocar couldn't recover from a crash of the STM tip on the surface, an accident induced by a software crash that affected first the Tsukuba team LT-UHV 4-STM controlling computer of their STM scanner just one hour after the beginning of the race. The two teams were racing on the shared gold surface. As a consequence of the crash, the Tsukuba team lost its nanocar and the spares molecules prepared and stored beside the race track a week before the starting of the race [10,11]. After 20 hours, by the time the team had cleaned again its portion of the Au(111) surface and placed another nanocar on the track, a second software crash occurred on their controlling computer.



Team	Rice-Graz (team leaders: Leonhard Grill, James Tour)	Basel (team leader: Remy Pawlack)	Ohio (team leaders: Saw-Wai Hla, Eric Masson)	Dresden (team leader: Francesca Moresco)	Toulouse (team leader: Gwénaël Rapenne)	Tsukuba (team leader: Waka Nakanishi)
Surface	Ag(111)	Au(111) (shared)	Au(111)	Au(111) (shared)	Au(111) (shared)	Au(111) (shared)
Propulsion mechanism	dipolar	inelastic	dipolar	inelastic	inelastic	inelastic
Driving distance	1 000 nm in 29 hours	133 nm in 6 hours	43 nm in 29 hours	11 nm (first hour)	25 nm by pulling (not allowed)	1 nm (first hour)
accidents	–	–	–	Molecule was stuck on a defect; Molecule destroyed	Molecule jumped on the tip	Motor blocked

Table 1: *The official Nanocar Race I ranking table published after the race in Nature (which was also sponsoring the race). The molecular structure of each competing molecule-vehicle is indicated (about in relative scale) with all the blue molecule competing on Au(111).*

The Tsukuba team was thus not ranked, but it was awarded the 'fair play' prize. After the race, a detail analysis of the controlling computer allocated by the organizers to the Tsukuba team demonstrated how the computer memory filling up during their training during 2 weeks was not cleaned enough before the race. It was a software problem for this computer since all the 6 controlling computers (one per team) were all cleaned up before the race. For a reason unknown yet, the Tsukuba computer refused this full cleaning operated the evening before the race.

The Toulouse team was also not ranked because the only way to move their nanocar during the race was to pull and push it with the STM tip, because the molecular wheels adhered too strongly to the Au(111) surface [12,13]. Pushing and Pulling, was against the Nanocar race rules. They covered 25 nm in 3 s before their nanocar jumped on the tip. However, they received a special mention for the stunning STM images of their nanocar (Figure 6c) recorded during the race [13].

4. HOW TO DESIGN BETTER MOLECULE-CARS?

During the training session and also during the race, it became clear that the organic synthetic chemists should be happy that some of the rather small molecules engaged in the competition could be controllably driven for so long and so far on a metallic surface. Each molecule-vehicle have supported thousands of electrical excitations without suffering major damage and with almost no ‘sticky finger’ effect, that is, unwanted interaction with the STM tip. Only the Toulouse molecule-car was found very likely to jump on the tip apex, because of the pulling-pushing forbidden mode of manipulation adopted by this team which is requiring a very small tip apex to surface distance [13].

An important lesson coming from the race is that an efficient design of a molecule-vehicle cannot rely only on the intuition of synthetic chemists. Usually, they are trying to design their molecule-vehicle like an ultimate miniature version of a macroscopic car. This generally leads to rather large molecular structure with large wheels and chassis. This is in the art of organic chemists to provide such beautiful molecular structure [1]. But they not always seem to be adapted to a good on surface driving at the nanoscale.

Furthermore, small molecules are easier to pilot on the surface than large ones. This opens an important debate on the chemical structure that a molecule-vehicle must have to be controllably ‘driven’. The beauty of the synthesis of a large molecule with a chassis, molecular wheels and a mechanical molecular motor is unquestionable. At the same time, the good performance of a molecule with fewer than 100 atoms, such as the Basel team nanocar (42 atoms) [7], are now analysed in details to get a clearer understanding on how a single molecule can be driven on a surface in a step-by-step way [7,9,10]. As observed largely during the training of the Basel team and during the competition [7], each step can be of the order of a few lattice constants of the metal surface. Sometimes more than 10 steps can be made following a single excitation if an electrostatic effect is involved, as in the case of the Rice–Graz nanocar [6].

As shown by the nanocars from Basel, Dresden and Tsukuba, the propelling motor does not need to be apparent. Intramolecular quantum effects involving very specific ground and first electronic excited states must be harnessed to be able to pilot a single molecule on a surface for a long distance. The success of the smaller molecules in this respect requires a detailed analysis to understand the role of inelastic tunnelling in their propulsion and to identify the electronic states involved. This insight will help equipping larger molecules, such as the Toulouse and Ohio nanocars, with a reliable propulsion system taking full advantage of their electronic excited states [7,9,10]. The question of why the mobile parts of the Tsukuba molecule showed a tendency to stop after a few current pulses, even though there were no apparent changes in the electronic structure of the molecule, needs to be answered [10]. Quantum chemists will be the designers of the next generations of nanocars, in close collaboration with molecular chemists. This is the reason why the organizing committee of Nanocar Race II had decided to ask to have a quantum chemist in each team and to declare it in the pre-registration form.

5. THE NEW INSTRUMENTATIONS DEVELOPED FOR THE RACE

During the preparation of the race and during the training, surface physicists learned much in terms of instrumentations. Depositing four very different molecules on the same surface (8 mm in diameter) at four different locations was a challenge for the P2.1 organizers. It took two years of hard UHV designs and constructions to set up the required UHV devices [5].

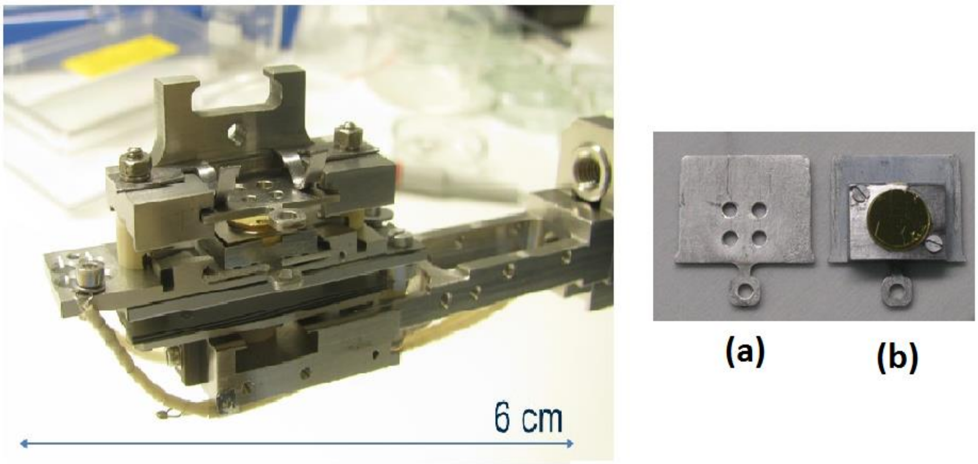


Figure 5: *A detail photo of the specific masking evaporation device designed specifically for Nanocar Race I. The Au(111) sample pastille is clearly visible in the centre of the support together with a molybdenum mask here with 4 holes. Both the Au(111) sample holder and mask holder can be moved out of this support in the UHV. Notice that the Au(111) was mounted on a dedicated heater to clean the complete Au(111) surface for example for the on-surface chemistry required by the Dresden molecule-vehicle supramolecular assembly [9]. (a) A top view of a 4 hole mask. (b) A top view of the Au(111) sample clipped by a tantalum foil on its sample holder.*

As presented in Figure 5, a dedicated and completely new UHV masking system was developed to deposit different molecules on different zones of the same surface. It consists of a set of molybdenum ultra clean mask where a 2 mm hole had been pierced a different location per mask (Figure 5a). All the masks were stored in a specific UHV carousel ready to be used and positioned over the Au(111) 8 mm sample whose support was supporting the race. The distance between this surface and the bottom part of each mask was about 3 mm to avoid any large diffusion of the molecule-vehicles through the 2 mm hole of the mask. This type of UHV device (Figure 5) is now used in the field of on-surface chemical synthesis, where a multiple step on-surface synthesis is now possible [14].

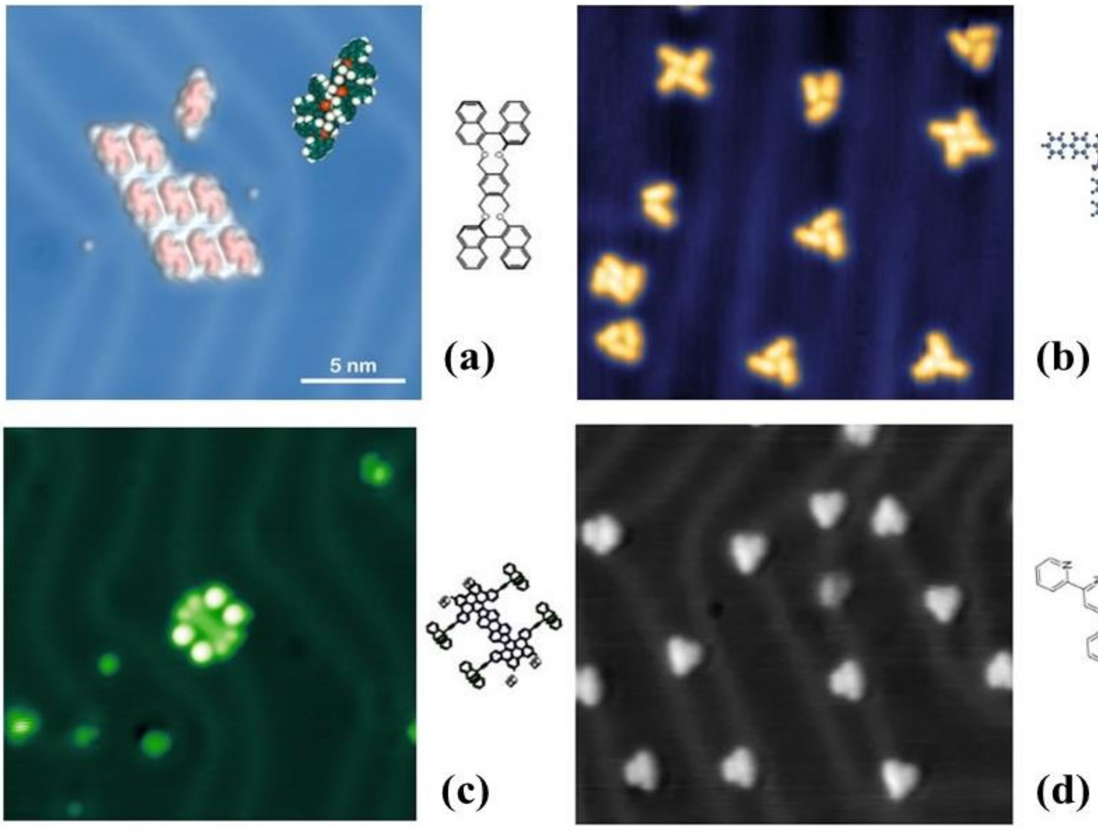


Figure 6: *High resolution constant current STM images recorded during Nanocar Race I by (a) the Tsukuba [10], (b) the Dresden [9], (c) the Toulouse [13] and (d) the Basel [7] teams on the LT-UHV 4-STM at the same time by each respective driver. Each team had selected each own colour code. Since the sample is grounded on the LT-UHV 4-STM, each team can adopt different bias voltage and feedback tunnelling current intensity during the race. Only the pulsing bias voltage rate was limited during the driving to avoid cross talk between each scanner n the LT-UHV 4-STM.*

Demonstrating that four low-temperature STM tips can be simultaneously used to measure on the same surface by four independent users was a real tour de force (Figure 6). In particular, the tip-to-tip apex distance was maintained very small, less than 4 mm during all the competition. The configuration used during the race for the four tips is unique: each tip was perpendicular to the surface to mimic the tip configuration of a standard LT-UHV STM. The picometre resolution and the ability to perform atomic-scale manipulation were preserved for each tip, independently of the manipulation protocols employed by the pilots. This impressive demonstration holds promise for the nascent field of atomic-scale construction of electronic circuits and of the molecule-by-molecule assembly of mechanical machinery so important for the MEMO project.

The exploratory work performed to prepare the first nanocar race will be in fact be very useful during MEMO to measure for example the propagation of a rotation motion along a train of molecule-gears. In this case, the tip-apex to tip-apex distance in a 45° configuration (as presented in Figure 1b and 1c) must be pushed towards 100 nm. The molecular manipulation capability will be maintained for MEMO by reserving a 90° perpendicular oriented STM tip for precise single molecule manipulation like mounting a single molecule-gear on its single metallic atom axle as demonstrated in WP1 MEMO year 1 on the LT-UHV 4-STM.

Interestingly and even if a computer crash occurred twice during the race, the hardware of the P2.1 Toulouse LT-UHV 4-STM microscope worked perfectly during the 30 hours of the competition and during the two weeks of intense training before the race. This is very important since for single molecule mechanics, multiple STM tips are required to work on the same surface for constructing the mechanical machinery and to experiment their functioning. It was for example noticed during the training phase of the race that liquid He refilling for the 36 hours retention time on the P2.1 Toulouse LT-UHV 4-STM can be performed without losing the working area within about 10 nm. This is effective as soon as all the 4 tips are retracted during this filling from the surface by less than 100 nm. The construction sequence of a complex machinery can therefore be performed for more than a week before the study of its functioning.

6. CONCLUSION

A worldwide audience followed the Nanocar Race I event. It was broadcasted live and it attracted more than 100.000 viewers at peak times over 30 hours. It was a true scientific experiment offered free and live to anyone interested over the planet. All the movies recorded during this Nanocar Race I are available free on http://nanocar-race.cnrs.fr. It is basically a collection of more than 40 Youtube movies with interviews of the sponsors and the teams, together with nice sequences recorded during Nanocar Race I. More than 200 media around the world have reported the event including TV broadcasting and radio interviews. The Japanese media were particularly interested with special show prime time on NHK and a direct show via skype from the Nanocar race control room to the Tokyo Science Museum on the early morning of April the 29th, 2017.

As evidenced from the publication list below, 5 teams over the 6 having participated, reported their finding during the race in high impact factor journals. Some of them are continuing to report the event during scientific conferences all over the world. The technology and scientific impact of Nanocar Race I is continuing in our days boosted now by the announcement of Nanocar Race II in 2021 (see MEMO Year 1 WP5.3).

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