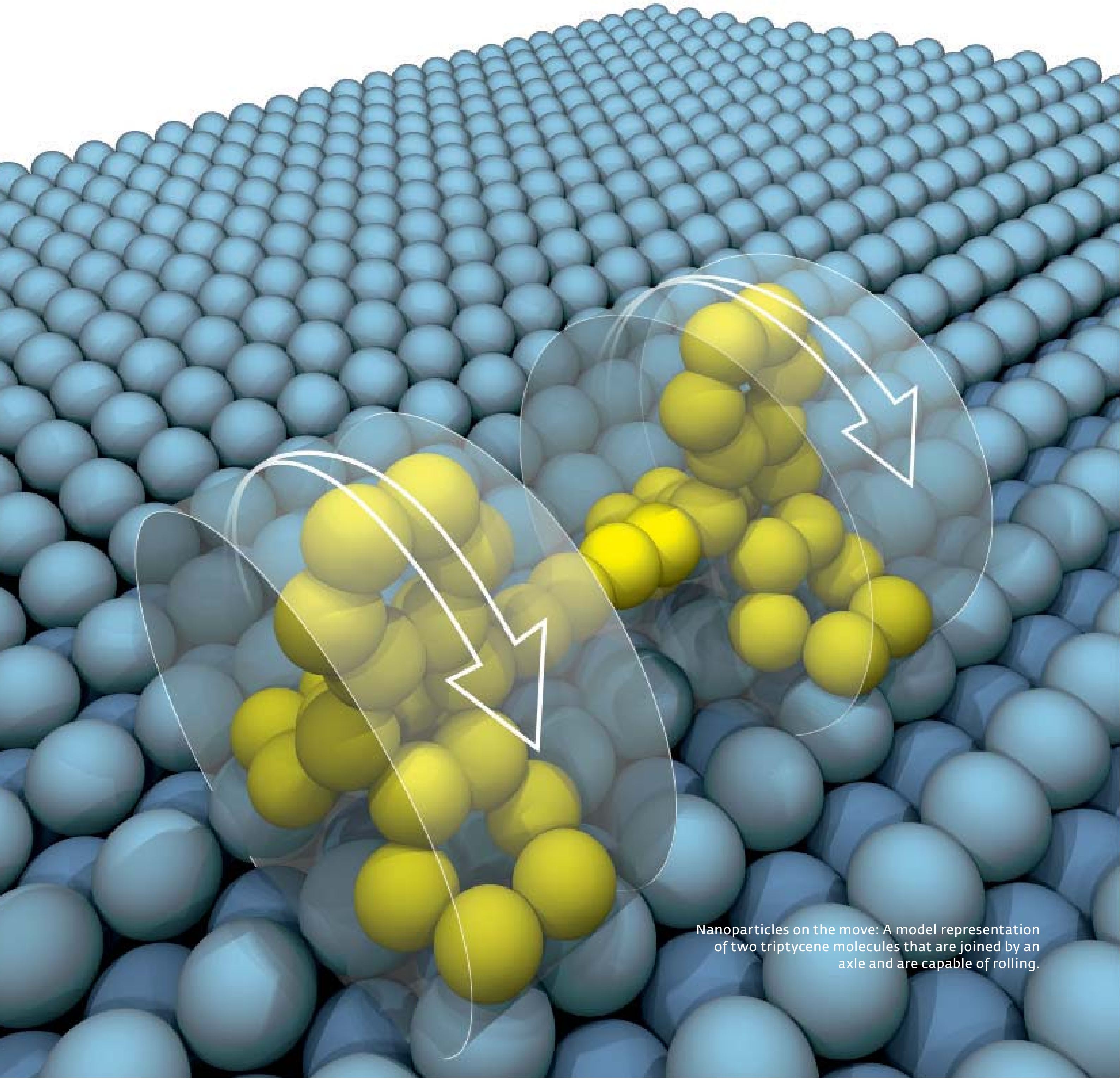
The Nanoworld
Is Starting to Roll



Nanoparticles on the move: A model representation of two triptycene molecules that are joined by an axle and are capable of rolling.

Imagine vehicles that are just a few nanometers large and that clean surfaces or build molecular structures like tiny vehicles at a construction site. To bring this idea, or that of molecular electronics, out of the realm of imagination and into the real world, physicists working with **Leonhard Grill** at the **Max Planck Society's Fritz Haber Institute** in Berlin are investigating the physics of the nanoworld – and they enjoy taking turns at the wheel

TEXT **ALEXANDER STIRN**

Not many physicists can claim that they reinvented the wheel, but Leonhard Grill can without any hesitation. Admittedly, his wheel isn't particularly large, it rolls only with extreme reluctance, it has no tires, and it isn't even round. It does, however, have one very special quality to offer: Grill's discovery is the world's smallest rolling wheel.

Leonhard Grill, a researcher in the Department of Physical Chemistry at the Fritz Haber Institute in Berlin, works with nanostructures – objects with dimensions in the range of millionths of a millimeter. The wheel that Grill developed in collaboration with chemists from the French Centre National de la Recherche Scientifique in Toulouse has, for example, a diameter of just 0.7 nanometers. It consists of a rigid axle, on the ends of which the researchers attached two triptycene molecules. The bulky hydrocarbons look a bit like three-bladed airplane propellers. As a result, the nano-wheel is somewhat ungainly when it rolls – but it rolls.

"The dream is to one day use such molecular building blocks to build complex structures with precisely defined functions," says Grill. Tiny wheels, axles and a chassis could form a nanocar. Wires, switches and transistors – each measuring just a few atoms – could come together to form a molecular circuit.

Currently, such nanomachines still fall within the realm of science fiction. No one can say whether they work or whether they can ever be built. And Leonhard Grill, an Austrian with a calm, sonorous voice, would be the last to encourage unjustified expectations. But Grill, very much the basic researcher, finds the search for such systems extremely interesting. The Berlin-based physicists are therefore working to characterize a wide variety of molecule candidates. They are learning to move, manipulate and combine individual components to form ever more complex structures.

HOW MOLECULES CAN BE VIEWED AND MANIPULATED

It's a bit like Lego with molecules – the only difference is that Grill and his team can't see the building blocks, much less touch them. They must rely on technical support.

Leonhard Grill always has his most important aid in view: over his desk hangs a large poster that explains how the scanning tunneling microscope works. Gerd Binnig and Heinrich Rohrer, who developed the technology and were awarded a Nobel Prize for it, autographed the poster.

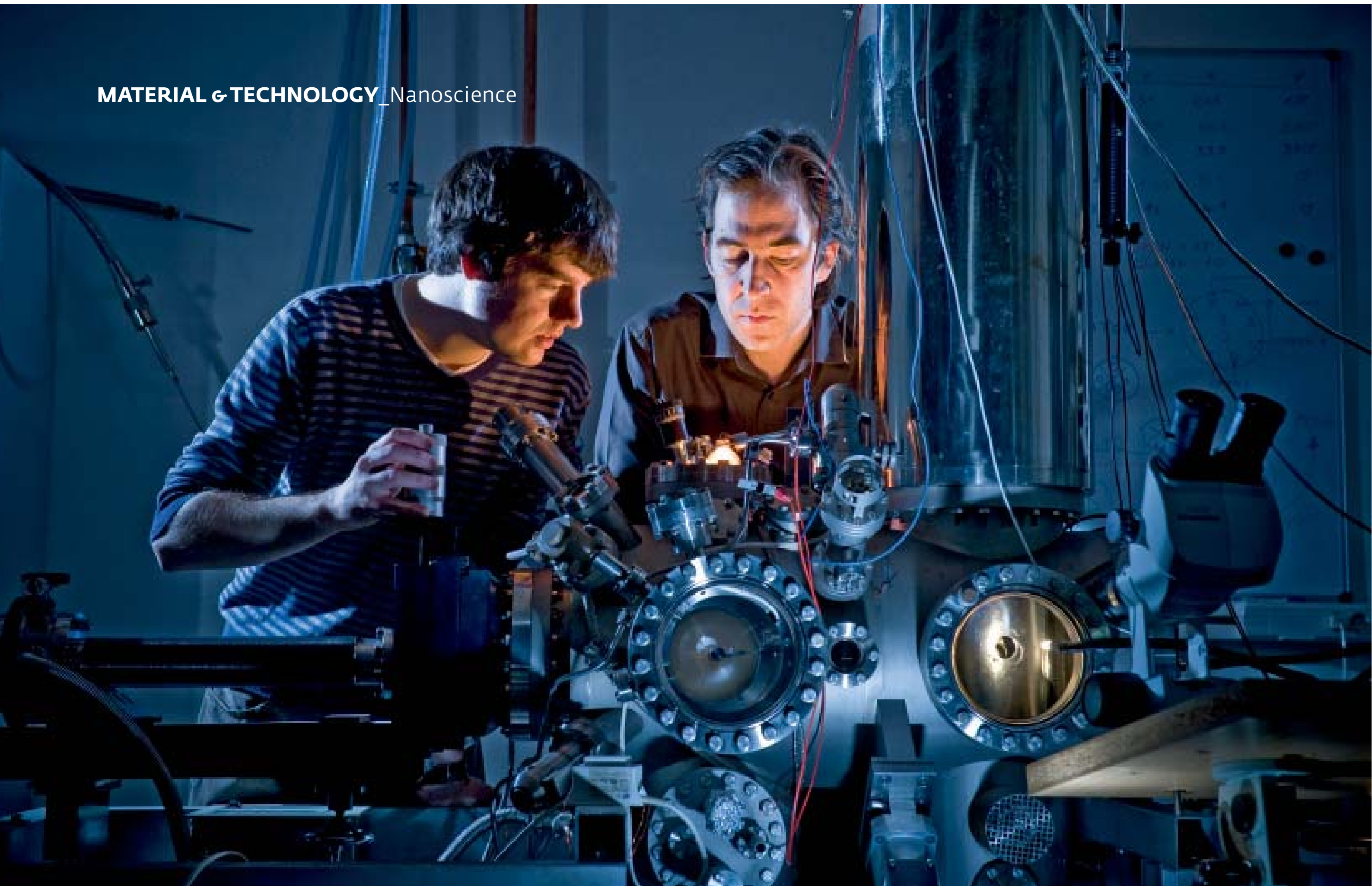
The real microscopes are two floors below, in the basement of the time-honored "Kaiser Wilhelm Institute of Physical Chemistry and Electrochemistry." Pumps hum, cables snake through the room, some of them wrapped in thick layers of aluminum foil. In their midst, two stainless steel machines gleam brightly. They appear to be made of cylinders screwed together arbitrarily – covered with numerous flanges and round peepholes.

Alex Saywell, a staff member in Grill's research group, sets a spindle at the end of the long cylinder in motion. With a metallic drone, it slowly pushes a sample into the scanning tunneling microscope. Saywell previously cleaned the fingernail-sized piece of metal, then bombarded it with ions and heated it. Now it isn't just shiny, it is absolutely pure. Later, custom-tailored molecules – components that the physicists want to analyze and use to begin their Lego game – will be deposited on its surface.

"The scanning tunneling microscope enables us to look at or analyze individual atoms," says Leonhard Grill. This is made possible by the microscope's fine metal tip, on which, ideally, just a single atom sits. At a distance of about one nanometer, it traverses the sample surface row by row. An electric voltage allows the physicists to measure how much current flows between the microscope and the substrate. "The ingenious trick of scanning tunneling microscopy consists in the fact that this current is extremely dependent on the tip's distance from the surface," says Grill. If, for example, it passes over a molecule on the surface, the current increases sharply.

A fully automatic standard scan takes a few minutes. A very good image may sometimes take 20 minutes to complete. In the meantime, a colorful image appears line by line on the at-

Photo: Claudia Döring



A machine that Leonhard Grill (right) and his team use to study nanomachines: Together with Alex Saywell, he transfers a sample from the preparation chamber to the measuring position in the ultra-high-vacuum system. There, the researchers inspect the sample with, for example, a scanning tunneling microscope. The great cylinder in the right half of the image contains the cryostats that are used to cool the sample.

tached monitor. The different colors represent the intensity of the measured current – and thus the contours of the surface. Even the untrained eye can recognize the individual atoms of the metal layer and the molecules lying on it.

But the scanning tunneling microscope lets the scientists do more than just look at the molecules: the fine tip becomes a mini finger that pushes the particles around. The first time this was done was in 1990, by physicists in the IBM research lab in Almaden, California, who wrote their employer's name with xenon atoms. Five years later, researchers at the Free University of Berlin succeeded in reproducing the silhouette of the Brandenburg Gate with individual carbon monoxide molecules. "Today, things like that are standard," says Leonhard Grill. "But it's good training for students, who then learn how manipulations work and what the limits of such games are."

So far, though, the small push with the tip has always made the molecules hop into their new position. The researchers never saw any rolling until Grill reinvented the wheel.

But how can physicists tell whether a molecule will hop or roll? And how can they prevent it from rolling off the shiny surface? Leonhard Grill grins: "The laws of physics that we know from everyday life don't help us in the nanoworld. There are very different factors at play there."

Take the wheel, for example: Once set in motion, a normal wheel just keeps rolling – assuming it doesn't sink into the mud. Its mass and the associated inertia keep it moving. In the nanoworld, in contrast, masses are so small that gravity and inertia no longer have any influence. Instead, electrostatic and chemical forces take over.

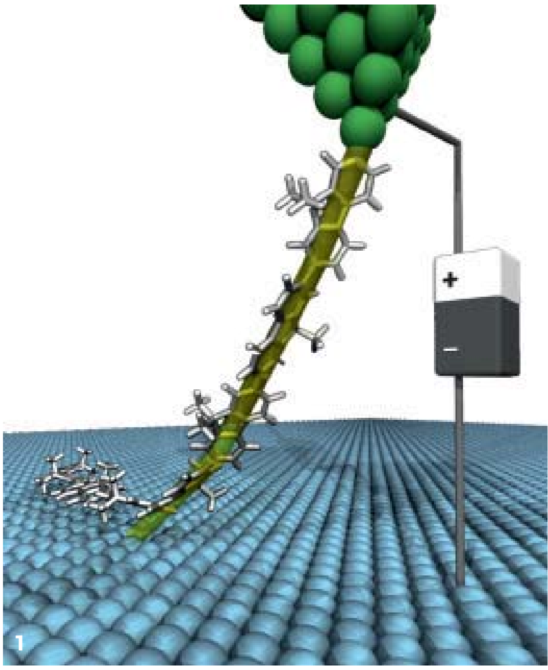
Grill's triptycene wheel, for example, is so strongly attracted by the slightly corrugated copper surface that it must be pushed forward continuously with the tip of the scanning tunneling microscope – similar to a finger rolling a six-sided pencil across a desk. And just like the finger, the tip of the microscope starts out behind the molecule wheel. While pushing, it invariably passes over the wheel to land in front of it – where the forced rolling then comes to an abrupt halt.

100-YEAR-OLD WALLS PROTECT THE MEASUREMENTS

Such processes are reflected in the measured current intensity of the scanning tunneling microscope: when molecules hop to flee from the tip, the current first spikes, then suddenly drops, like a sawtooth. In contrast, when they roll, a wave motion is seen that matches very well with the wheel's propeller form. "It was very exciting the first time we saw something like that," recalls Grill. "And it also shows that, despite all of the playful elements, one can learn a lot about the physics behind the molecular building blocks if one looks very closely."

Such insights, however, are possible only when the tip can be positioned extremely precisely. There can't be any

Photo: Norbert Michalke



1 With the tip of the scanning tunneling microscope, a nanowire is raised up to measure how its resistance increases atom by atom.

2 Leonhard Grill with a dismounted measuring head of the scanning tunneling microscope.

3 On the support, the researcher mounted a metallic sample that is visible here as a circular copper platelet.

Graphic: Fritz Haber Institute; photos: Norbert Michalke (2)

disturbances. But with a required precision of one hundredth of a nanometer – one tenth the diameter of a hydrogen atom – thermal motion alone becomes an utterly insurmountable obstacle.

The microscopes must therefore be highly cooled. The thermometer on the sample that Alex Saywell first briefly heated and then put into the ice-cold stainless steel cylinder shows minus 247 degrees Celsius. A couple more minutes, then it, too, will have the temperature of liquid helium – nearly 5 degrees above absolute zero.

On top of this, the pressure is infinitesimal: the barometer shows 8.7 x 10^{-12} millibars, or about ten trillionths of normal ambient pressure. “That’s better than the vacuum in the orbits of satellites,” says Grill. The atmosphere in the microscope is so thin that the researchers can take measurements for weeks without any air molecules sticking at the surface and disturbing the images.

Also the current intensities require the utmost precision. The scanning tunneling microscope measures currents that range in the billionths of amperes and lower. Even slight disturbances in the network – for example suddenly turning on an energy-hungry pump in the next room – would have devastating consequences. The electricity for the microscope is thus supplied by a power pack that is also used to ensure uninterrupted electricity supply for the servers. Grill clicks on a small diagram on the monitor of the microscope – it shows no disruptive frequencies.

The measurements immediately become useless when the instrument begins to shake. But the physicists in Berlin are lucky in this regard: the Fritz Haber Institute is located in an exceptionally calm villa neighborhood in Dahlem. The subway is far enough away, the foundation of the 100-year-old building is massive, and the walls in the basement are a good meter thick.

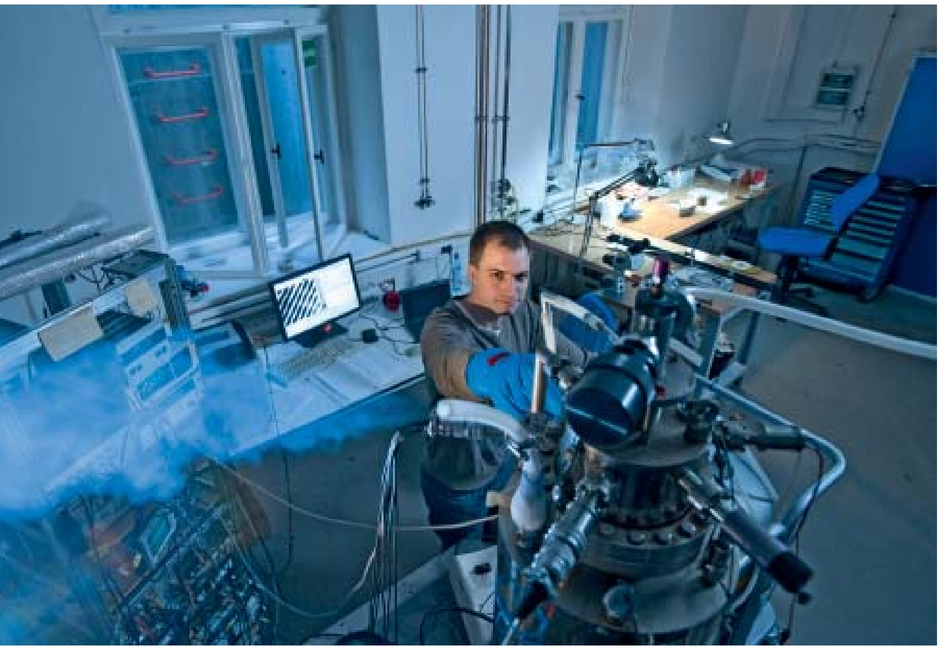
ROLLING MOLECULES AS NANOWHEELBARROWS

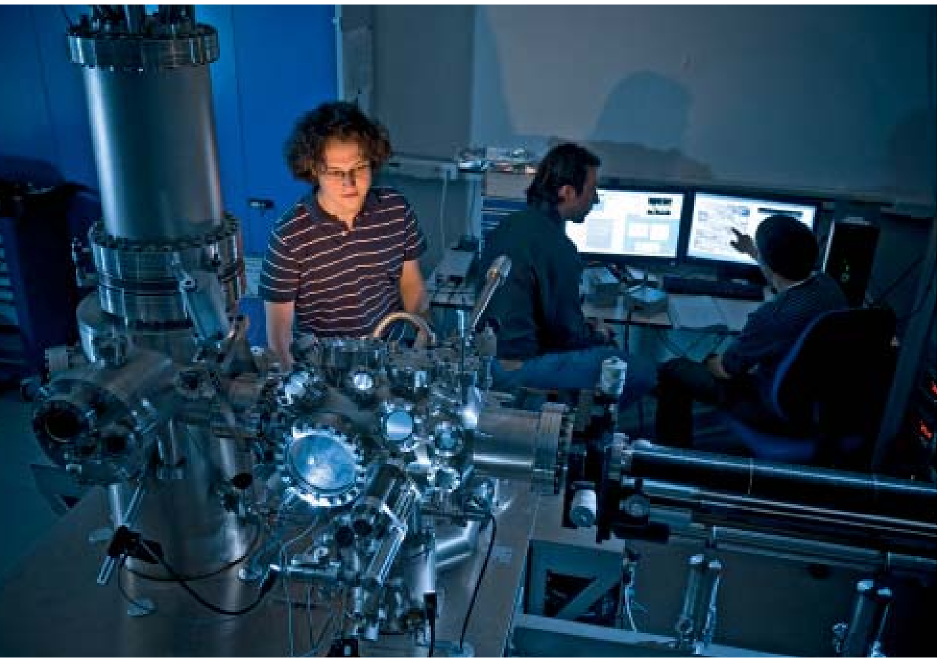
Nevertheless, Grill and his team leave nothing to chance: when they take measurements, they turn off the light and the humming vacuum pumps. The room doesn’t even have air conditioning, as the airflow could cause the delicate stainless steel apparatus to vibrate. “Evening is usually the best time to take measurements, when both the building and the staff have quieted down somewhat,” says Leonhard Grill. Then one can also reinvent the wheel.

But why do nanomachines need to roll in the first place? After all, the greatest advantage of macroscopic wheels – the significantly reduced frictional resistance – becomes far less important in the nanoworld. “A molecule with wheels can move in only two directions – forward and backward. Compared with an undirected diffusion, that would be a great step forward,” says Grill. Rolling molecules may also have the potential to surmount small steps on an atomic surface – one of the great obstacles to date in the spread of the tiny particles.

Furthermore, it is hoped that individual wheels are just the beginning. In the basement of the Kaiser Wilhelm Institute, Grill and his team have also examined molecular wheelbarrows – specially designed molecules that roll and that are intended to transport atoms one day. Even a nanotrain with several cars was already at the starting line. Unfortunately, the physicists couldn’t discern any rolling motion for either of the vehicles. The molecules were probably simply too strongly attached to the surface. “For us, this means that, together with the chemists, we must continue to tinker with the molecular design,” says Leonhard Grill.

However, the Berlin-based researcher is interested in more than just mechanical problems. In Grill’s office, where the windows look out on Fritz Haber’s former villa, hang two covers





top: Replenishing the coolant: Matthias Koch fills the cryostats with liquid nitrogen to bring the device to around minus 200 degrees Celsius. Then liquid helium is used to cool the sample to about minus 268 degrees Celsius.

bottom: Ph.D. student Johannes Mielke prepares a sample in the ultra-high-vacuum system.

of the journal Nature Nanotechnology. The first one shows the molecular wheels, the other a couple of inconspicuous orange spots against a black background. They are nano-building-blocks that could one day change the computer world.

"In molecular electronics, it's all about miniaturizing circuits down to the level of atoms," explains Grill. Individual molecules are designed to form switches, wires, transistors and all the other necessary components, and to arrange in predefined architectures by self-organization – that is, without being directed by any external force. Researchers call this a bottom-up process. The tiny dimensions would mean short paths and thus extremely short computing times. The components would be cheap to produce, and would require extremely little electricity – after all, single electrons are already sufficient to trigger the desired functions.

So far, however, the semiconductor industry is taking precisely the opposite route: it is trying to shrink its chips top-down by etching ever smaller structures into the semiconductors. Moore's law, originally an empirical formula that states that the number of transistors on a computer chip doubles every 18 months, has long since become a target throughout the industry. But the miniaturization is slowly reaching its limits: transistors that are just a few atom layers thick can hardly be produced reliably with lithographic processes.

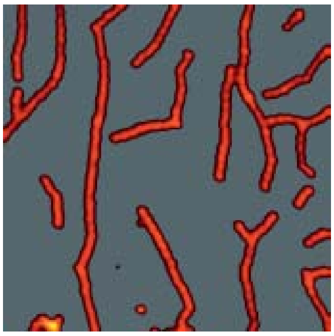
Then – so the nanophysicists hope – molecular electronics will have its day in the sun. In any case, Grill and his team have already built the first wires. This undertaking was aided by molecules that chemists at Berlin's Humboldt University custom designed especially for this purpose. The molecule designers used carbon compounds and blocked their reactive arms with weakly bound halogen atoms.

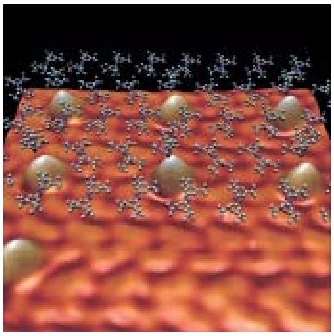
THE NANOWIRES ARE STILL VERY POOR CONDUCTORS

When heated in the scanning tunneling microscope, the halogen bonds broke open as desired. The molecular building blocks searched – entirely on their own – for new partners. They recognized reactive groups and formed stable carbon chains following the architecture the researchers specified. "With this form of self-organization, we are essentially imitating what nature has been doing very successfully for millions of years: it builds molecules with incredible precision and flawlessness," says Leonhard Grill.

The autonomous molecular Legos result in wires that can be up to 100 nanometers long and extremely stable. The physicists noticed just how stable they can be when they played around a bit with the wires and pulled them across the surface. "That was incredibly easy, almost as if with a rope," recalls Grill. "So we also tried to pull the wires up." And indeed: using the tip of the scanning tunneling microscope, the researchers were able to raise their wires

Photos: Norbert Michalke (2)





left: Close-up of nanowires: The polymers were dyed red in the scanning tunneling microscope image.

right: Dual image of molecular circuits: Images showing the structure of the azobenzene molecules are superimposed on a scanning tunneling microscope image. The researchers used an electrical impulse from the microscope tip to switch individual molecules. This caused their structure to change at distances of 3 nanometers, and they then appear as dents in the microscope image.

by 20 nanometers – and they didn't break. This even gave them the opportunity to measure the current flow in the molecular wires for the first time.

In doing so, it became clear that, unlike in conventional wires, resistance increases exponentially with length – not necessarily a good sign for molecular electronics: "It still isn't a wire in the traditional sense," says Leonhard Grill, "as it's a very poor conductor. But at least we were able to show that electrons can be transported across such constructs."

The first ideas for nanocircuits are also already on the table. And once again, nature is the role model: In the eye, for example, there are two variants of the retinal molecule, called isomers. When light hits the retina, the one form changes into the other, the nerve cells receive an impulse, and the brain is notified.

That is exactly what the physicists in Berlin have realized on surfaces: They use light or heat to start the isomerization. They open a molecular circuit and then close it again the same way – a reversible process.

Alternatively, the scanning tunneling microscope itself can be used as the trigger: although very little electricity flows between the tip and the sample molecule, on the nanoscale, a few electrons are sufficient to produce a high current density that is great enough to trigger the isomerization and thus activate the molecular circuit.

"The next major goal now is to couple the various systems – for example a circuit with a wire," says Leonhard Grill. And then? Will the molecules later automatically join together to form a tremendously powerful and simultaneously efficient supercomputer?

USING THE LEGO PRINCIPLE: LEARNING BY BUILDING

Leonhard Grill, the realist, shakes his head. "I can't imagine that we can get a complete chip with its millions of molecules to independently grow into a highly complex architecture." If molecular electronics should one day actually prove itself, then most probably in combination with the current chip technologies. But then new and maybe even revolutionary applications may be possible – for example in sensor technology.

And the nanocars that have long been driving across the screen in every science-fiction B-movie already? Grill laughs. "It's really difficult to predict applications, especially in a field such as nanoscience, in which completely new effects occur." After all, thousands of years ago, when the wheel was first invented, no one had ever thought about the balance spring of watches or the drive train of electric cars, either.

So it's very possible that nanomachines will one day clean surfaces, transport molecules or build simple structures – but Grill and his team are focusing on other things. These researchers follow the Lego principle: No one can say exactly what the end result will be when all components have been mounted. What matters is that the building process brings new insights.

"In any case, we aren't doing this because we would like to have a molecular chip or a nanocar in 30 years," says the 40-year-old, and looks out the window. "We do this because we find it interesting, because we want to understand what happens. But most of all, we do it because we are curious." ◂

GLOSSARY

Scanning tunneling microscope
A very fine, electrically conductive tip scans a likewise electrically conductive sample surface. Since the tip does not touch the sample, electrons tunnel from the sample to the tip. The tunneling current that flows in this process is strongly dependent on the distance between the sample and the tip. This makes it possible to determine the surface structure.

Bottom-up
Materials scientists borrowed this term from the field of software development. They use it to refer to a process in which small construction units combine to form larger structures due to natural physical or chemical forces.

Top-down
The reverse of the bottom-up principle: smaller structures are developed from a larger system, such as a silicon wafer.

Retinal
Together with the protein opsin, this forms the rhodopsin of the retina. Light changes the structure of retinal, causing opsin to be split off again and triggering a signal cascade that results in a nerve impulse to the brain.

Isomerization
When a molecule changes its structure in that its atoms relocate, without atoms being taken up or released.

Graphic: Fritz Haber Institute (2)