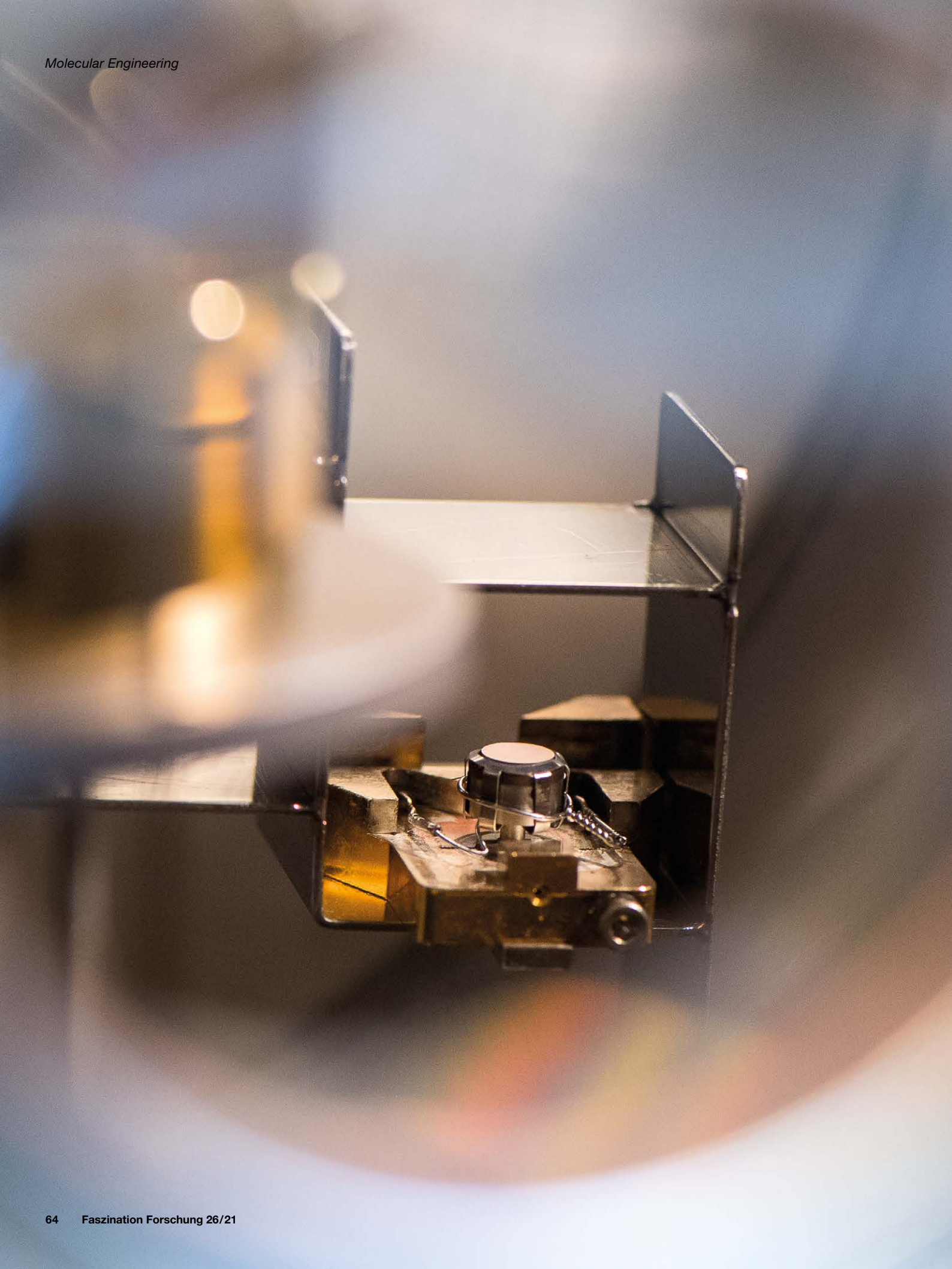

The **Molecular** Engineers

Time and again, individual molecules and atomically structured materials have been found to exhibit amazing properties. With elaborate ideas and sophisticated analytical methods, researchers around Willi Auwärter and Johannes Barth are currently exploring novel avenues towards future nanoelectronics, photonics, sensing, catalysis and quantum materials.

Kurzfassung · Langfassung: www.tum.de/faszination-forschung-26

Die Molekül-Ingenieure

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Aus Groß mach Klein: Heute werden Computerchips mit winzigen Schaltkreisen in greifbar großen Scheiben aus Silizium strukturiert. Aber auch umgekehrt lassen sich filigrane, elektrische Schalter auch aus einzelnen Molekülen zusammensetzen. Dieses Bottom-Up-Prinzip nutzen die drei Molekül-Ingenieure Prof. Johannes Barth, Dr. Joachim Reichert und Prof. Willi Auwärter, um mit ihren Arbeitsgruppen am Physik-Department der TUM neue Wege für funktionelle Einheiten zu gehen. Viele Anwendungen locken: Von Molekül-Schaltern und winzigen Sensoren über effizientere Lichtquellen und Energiespeicher bis hin zu reaktionsschnellen Materialien für Katalysatoren, Nanomotoren und sogar zu Funktionseinheiten zukünftiger Quantencomputer. „Mit unseren Experimenten betreten wir wissenschaftliches Neuland“, sagt Lehrstuhlinhaber Barth. So besteht ein erster Schalter-Prototyp nur aus einem einzigen Molekül aus der Gruppe der Oligophenyle. Parallel zum Bau neuer funktioneller Einheiten nutzen die Nanoforscher von Rastertunnelmikroskopen bis zu selbst entwickelten optischen Methoden einen ganzen Strauß an Analyseverfahren. Damit messen sie die Eigenschaften einzelner Moleküle oder komplexer metallorganischer Strukturen. Die Forscher legen so die Grundlagen für konkrete Anwendungen von der Nanoelektronik über die Photonik bis zur Katalyse – im Einklang mit den ambitionierten Forschungsprogrammen des Münchner Exzellenzclusters e-conversion und dem Munich Quantum Center sowie dem TUM Institute of Advanced Study. □

An atomically well-defined sample serves as the construction platform for custom-designed molecular nano-architectures investigated by high-resolution scanning probe microscopy.

Picture credit: Astrid Eckert/TUM

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“We are exploring innovative ways of preparing a paradigm shift.”
Johannes Barth

Picture credit: Astrid Eckert/TUM

Three scientists with a passion to build nanostructures using bottom-up construction principles. Biographies below from left to right.

Prof. Willi Auwärter

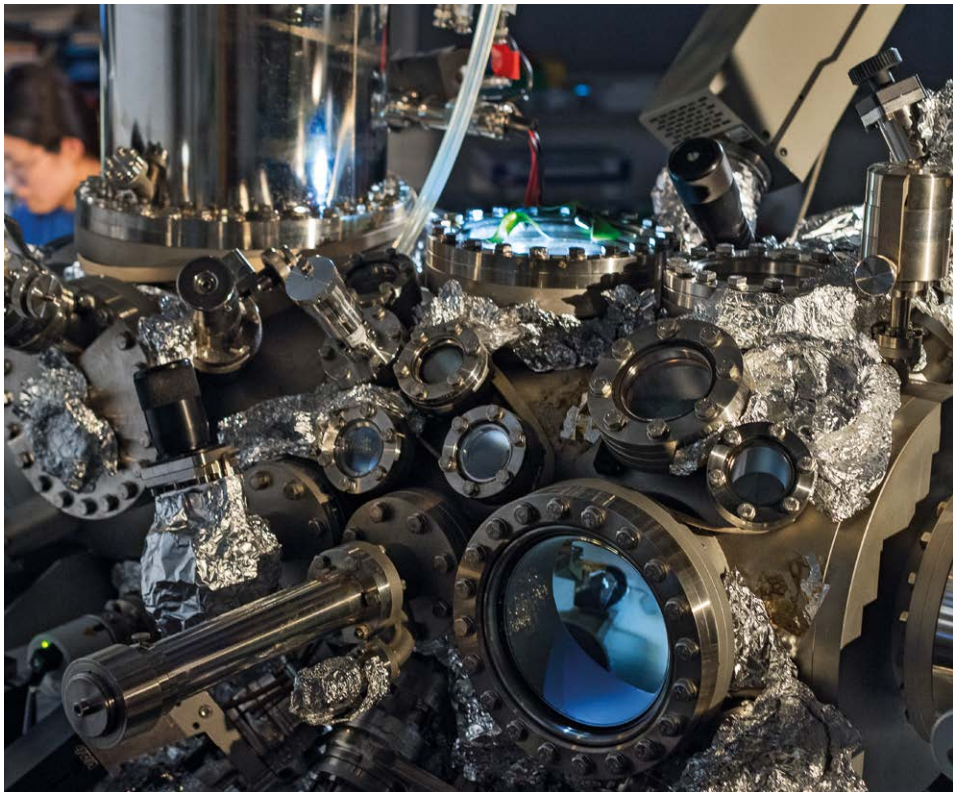
After being awarded his doctorate in physics by the University of Zurich in 2003, Willi Auwärter undertook research at the University of British Columbia in Vancouver and at the École Polytechnique Fédérale de Lausanne. He joined TUM in 2007, initially as a Fellow at the TUM Institute for Advanced Study and since 2015 as professor. His research was supported with an ERC Consolidator Grant and an Heisenberg professorship. His research group researches atomically precise molecular nanostructures and low-dimensional materials.

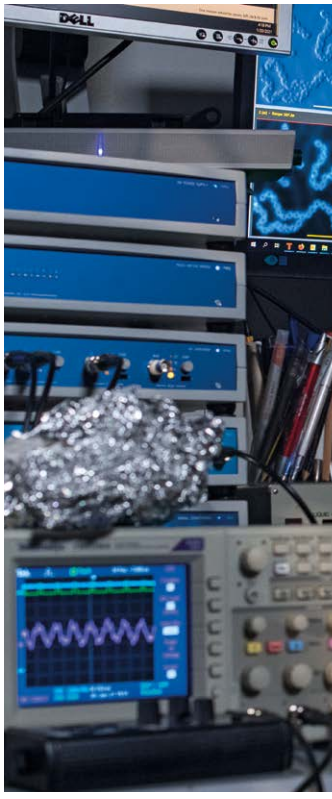
Prof. Johannes Barth

Physicist Johannes Barth was awarded his doctorate in physical chemistry in 1992 for work with Nobel Laureate Gerhard Ertl at the Fritz Haber Institute of the Max Planck Society in Berlin. After research visits at the IBM Almaden Research Center in San Jose and receiving the venia legendi at the École Polytechnique Fédérale de Lausanne, he was appointed professor of physics and chemistry at the University of British Columbia in Vancouver. Since 2007, he has been researching and teaching at TUM as chaired Professor of Surface and Interface Physics and has been Dean of the Physics Department for a number of years. He has received multiple awards and his work – supported in part by the renowned ERC Advanced Investigator Grant – deals with functional interfaces, surface chemical physics and molecular nanoscience.

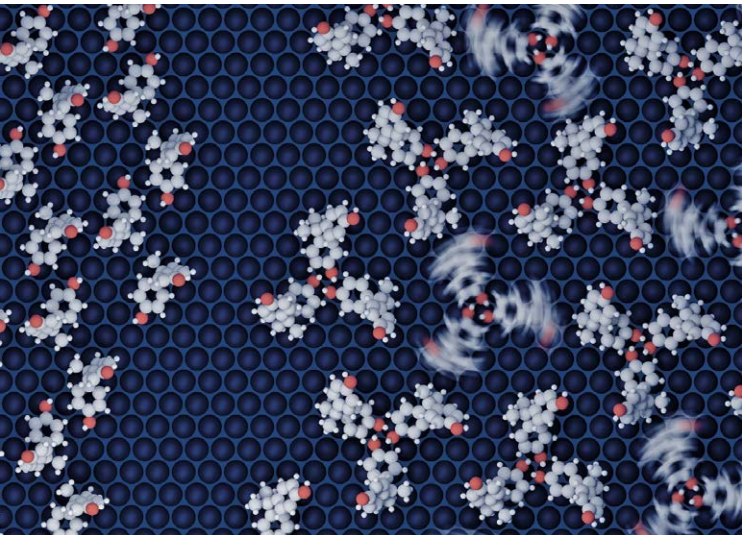
Dr. Joachim Reichert

Joachim Reichert earned his doctorate in physics from Karlsruhe Institute of Technology in 2003. He then undertook further research at the University of Münster and the University of British Columbia in Vancouver. Since 2007 he has headed a research group at TUM involved in analyzing and developing functional nanostructures and searching for potential components for the molecular electronics of the future.



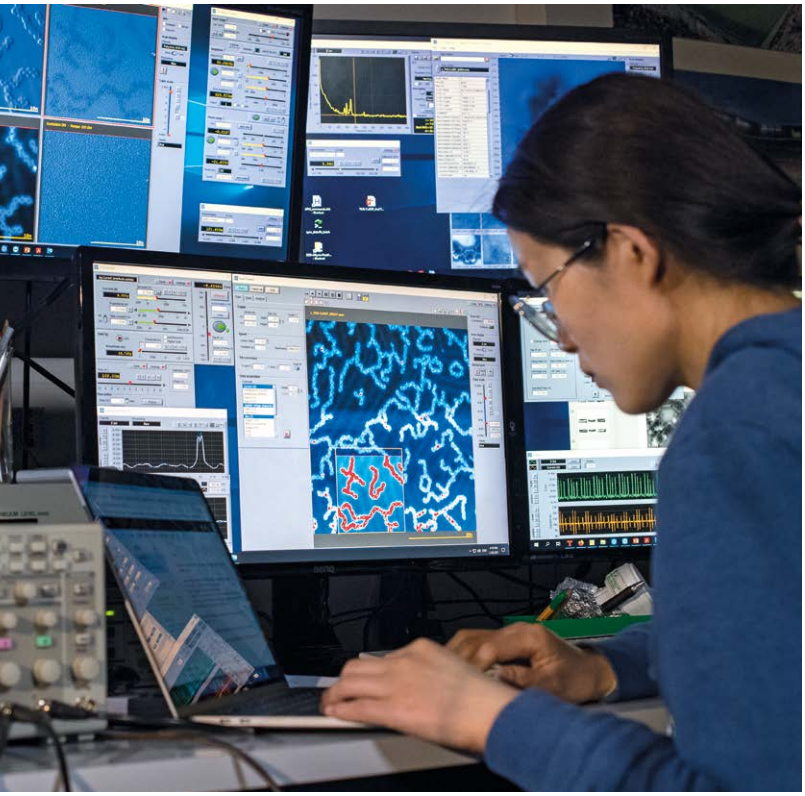


△ **To study individual molecules,** the team uses the atomic force microscope shown above and the scanning tunneling microscope.



△ **Computer generated image of a structure formed by bisphenol A molecules.** On extremely smooth surfaces (here: silver), three BPA molecules form trimers. Individual molecular trimers can be found rotating within a matrix of the same molecules, which remain static.

An electrical switch can hardly get smaller than this, consisting of just a single molecule from a group of chemicals called oligophenyls. Apply an electric charge, and the molecular backbone undergoes a controlled structural change. This modification is accompanied by a transition in the molecule's optoelectronic properties – the basis for jumping from 0 to 1 in digital switches. If a current with a voltage of a little more than a volt flows through this organic molecule, the three spatially rotated phenyl rings, each consisting of six carbon atoms, adopt a coplanar orientation – they all line up in the same plane. "Transiently, non-permanently charging the molecule transforms it from being an insulator to an electrical conductor and bestows a strikingly different optical response," explains Dr. Joachim Reichert, nanoresearcher in the Physics Department at TUM. In other words, the molecule suddenly acquires the ability to strongly scatter incident light, thereby providing an infallible means of determining whether the switching process has been successful.
Of course, there's a very long road ahead before we will be using legions of these molecules to produce extremely



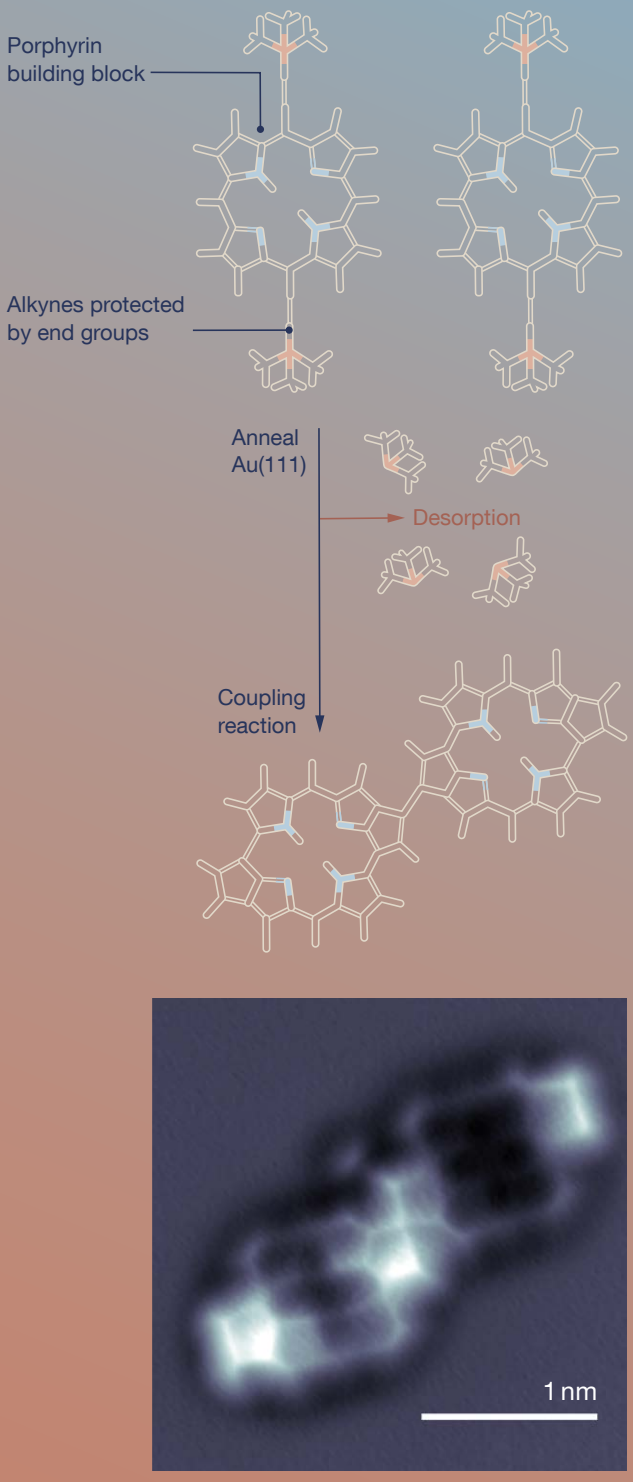
△ **PhD candidate Nan Cao** works at the scanning tunneling microscope. The screens show STM images featuring chain-like covalently bonded molecular structures (white/light blue) grown on a gold surface (dark blue). Selected molecular chains are highlighted in red.

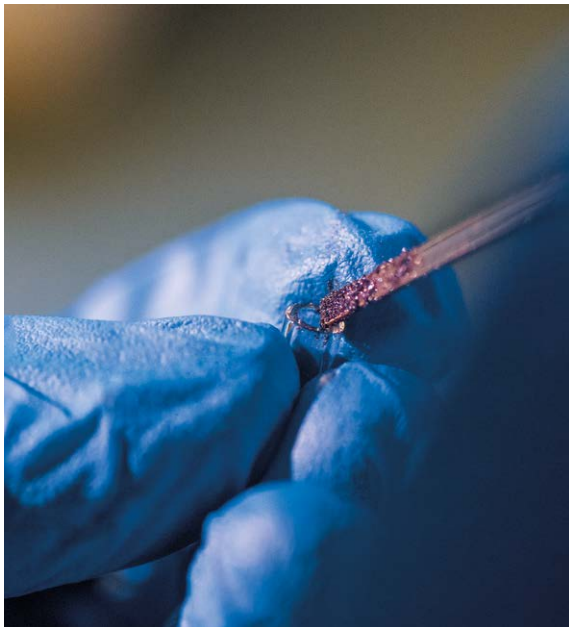
powerful processors. “At present, the switching process is still much more primitive than in a transistor,” says Reichert. But the foundations for molecular nanoelectronics have been laid, and chip manufacturers carefully follow this striking evolution. Conventional silicon circuits make use of structures just five to seven nanometers in size, but this technology is already butting up against its limits. Switches made of individual molecules – spanning just a fraction of a nanometer and many times smaller than current switches – could enable processors to continue their rapid miniaturization, or provide distinct useful features and response characteristics.

Bottom-up, not top-down: From molecule to material

“Our experiments take us into scientifically uncharted territory,” says Prof. Johannes Barth, who established the research unit. “We are exploring innovative ways of preparing a paradigm shift.” Barth and his colleagues are reversing the conventional process for developing new, versatile materials. Instead of forming smaller and smaller structures from large material blanks, they are ▷

▽ **Porphyrin building blocks form chain-like molecular structures** when they are deployed on a gold surface and tempered (thermal annealing). The protecting end groups separate and the remaining porphyrene structures form nanowires. The atomic force microscope image resolves the bonds between the individual “rings” and the newly established carbon-carbon linkage between them.



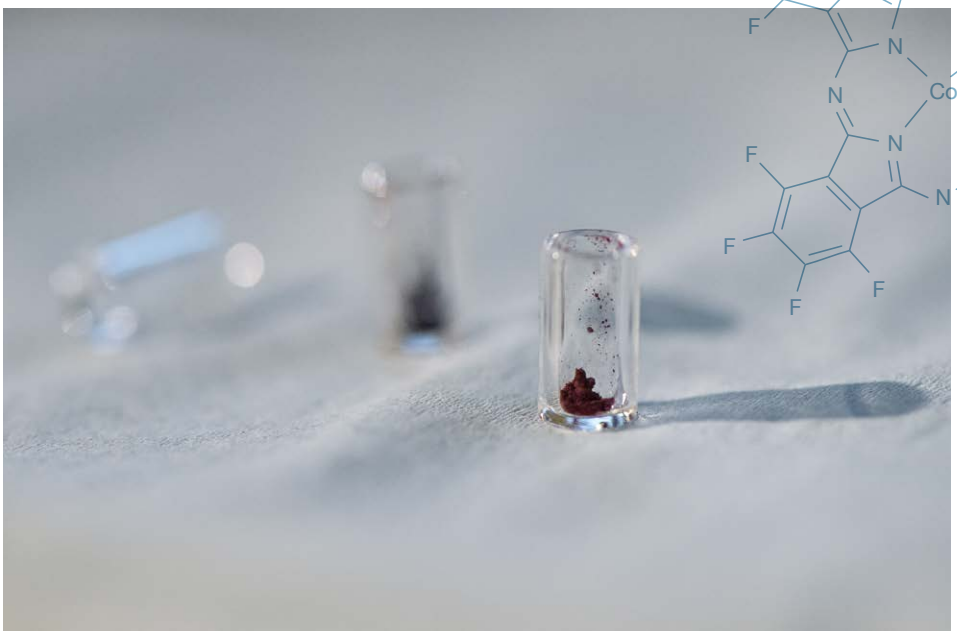


Preparatory steps to evaporate molecules onto the surface: Cobalt-phthalocyanine molecules are transferred from the container into a quartz crucible.

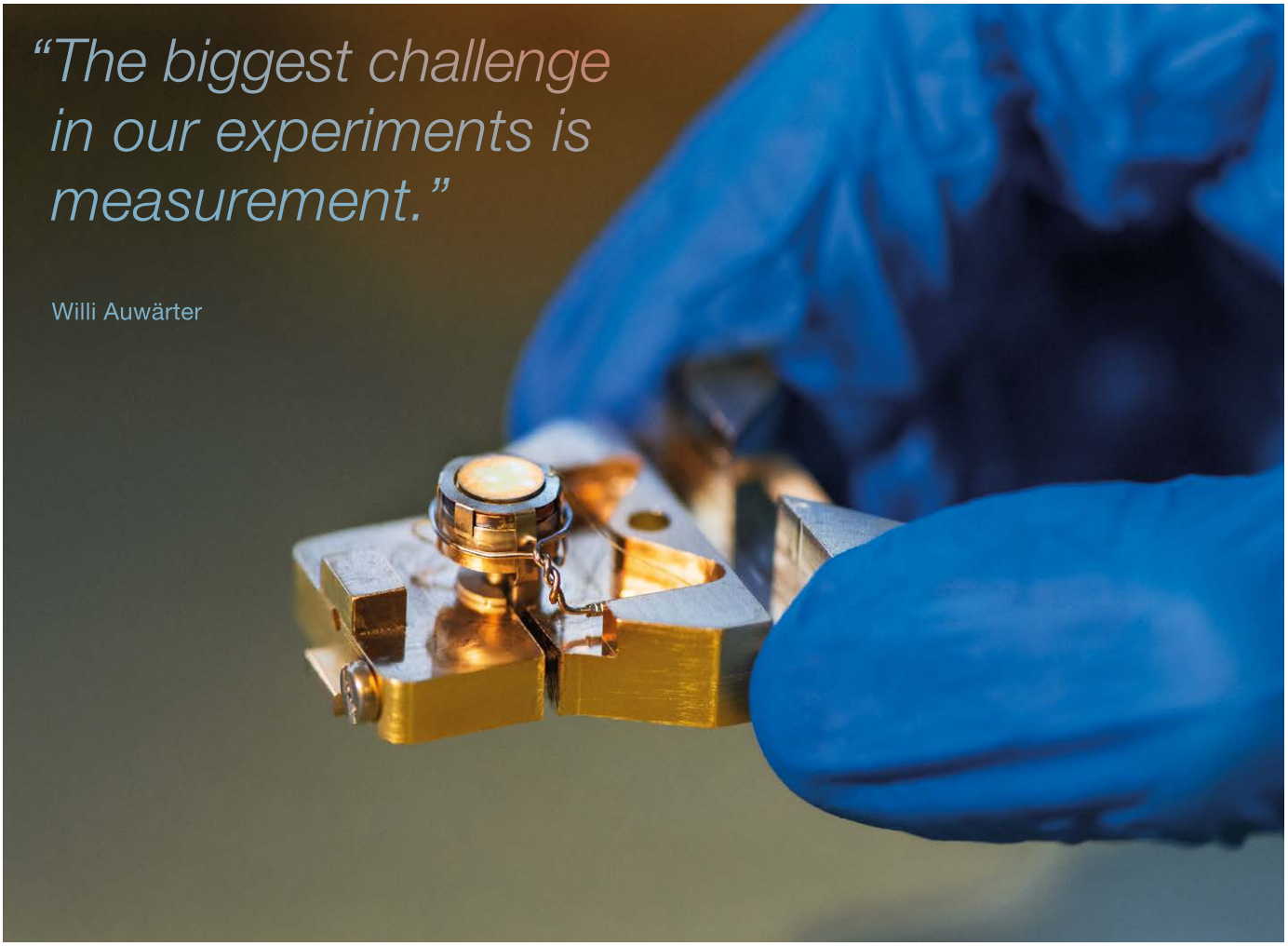
assembling functional units at interfaces molecule by molecule to produce hybrid systems with entirely novel properties. The technical jargon for this approach to nanotechnology is 'bottom up', in contrast to conventional 'top down' procedures. Nanoelectronics is just one of many potential applications for molecular engineering. These range from tiny sensors, more efficient light sources, solar cells and energy storage, to responsive, fast-reacting materials for catalysts, nanomotors and even the processing units for future quantum computers.

"There is no shortage of promising substances," notes Barth, who is at home both in chemical physics and molecular engineering. In addition to oligophenyls, for example, his group has also explored using the aromatic molecule bisphenol A for molecular switching. On extremely smooth silver surfaces, this molecule can be made to undergo controlled rotation about its axis like a radial rotor. Porous two-dimensional structures – in which atoms organize themselves into honeycomb lattices occupying a single plane, rather than a three-dimensional lattice – can be used as cages for holding individual atoms and molecules. "We have, for example, developed metal-organic networks with variable pore sizes in which we can incorporate and control either individual guest molecules or metal atoms," says Barth. Using their modular molecular system, the researchers can also create complex sandwich structures that promise to yield further novel properties. "For custom-designed molecules, we love to work closely with other expert research groups," says Barth, noting fruitful collaborations with chemists at the University of Basel, Karlsruhe Institute of Technology or Trinity College Dublin.

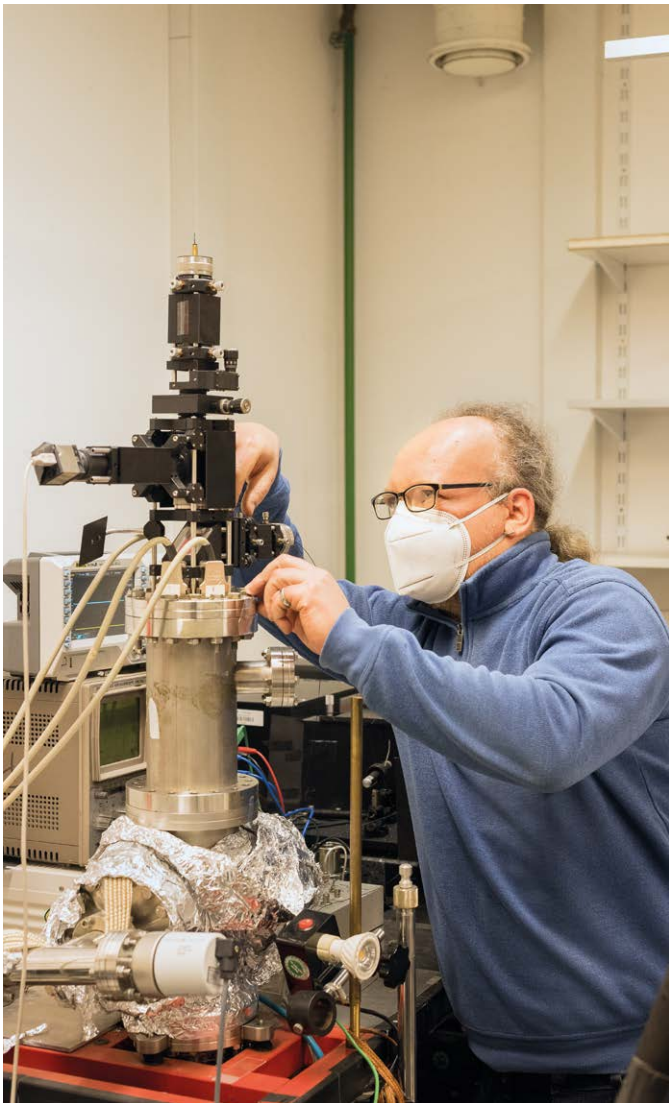
"Nonetheless, in building our molecular structures we receive comprehensive assistance from nature itself," says Barth. That's because almost all biological structures – from DNA strands to mitochondria to cell membranes – are produced through a process of self-assembly. The blueprint for these fundamental units of life lies in the molecules themselves. Our understanding of the spontaneous self-organization processes involved is constantly improving. It is this understanding that Barth and his colleagues are exploiting. By cleverly selecting the base chemicals, substrates and symmetries, they are able to induce molecules to arrange themselves into specific patterns. ▷



In a later step, the filled crucible is mounted in an evaporator, which will be attached to the ultra-high vacuum chamber. Even a small amount of molecules is sufficient to coat large surface areas.



Picture credits: Astrid Eckert/TUM Graphics: ediundsepp (source: TUM)

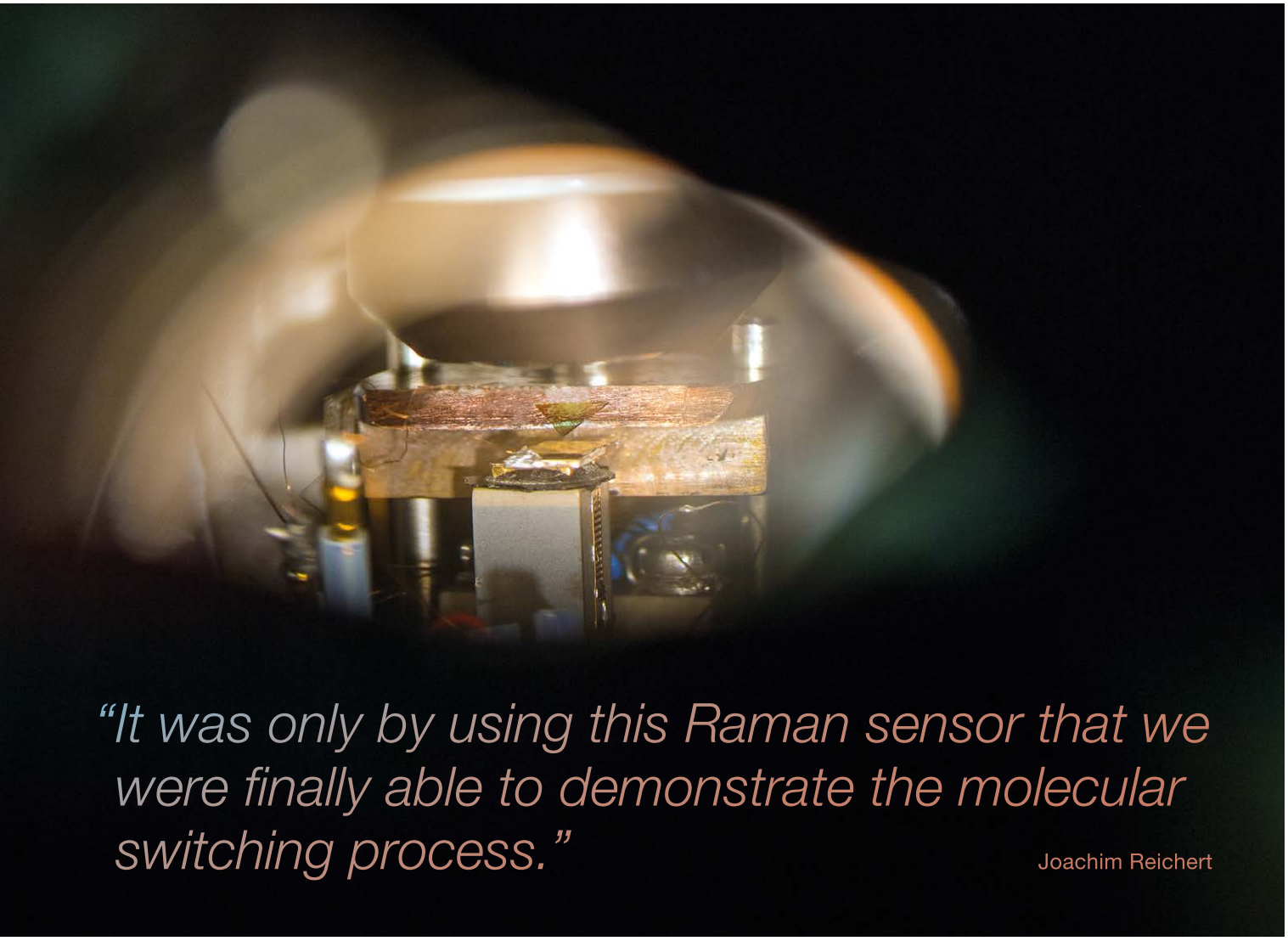


Joachim Reichert prepares a Raman scattering experiment to investigate the switching process of a single molecule contacted in a nanojunction between two electrodes.

New analytical methods

But synthesizing new functional units is just the beginning. To analyze the chemical and physical properties of individual molecules or complex metal-organic structures, molecular engineers need a whole host of analytical methods. Some are well established, some still need painstaking optimization and some haven't even been developed yet. "The biggest challenge in our experiments is measurement," says Willi Auwärter, Professor of Molecular Engineering at Functional Interfaces at TUM. In contrast to conventional analytical methods in chemistry, which typically deliver data averaged across ensembles comprising billions of molecules, "We are inspecting the properties of and the bonds formed by a single molecule," he explains.

Auwärter therefore uses extremely powerful imaging and atomic manipulation tools – the scanning tunneling microscope (STM) and the atomic force microscope (AFM). Both techniques utilize an atomically sharp microscope tip to address individual molecules. To minimize interference, experiments are carried out under vacuum conditions and at temperatures of around minus 268°C. By controling the tunneling current between the surface and the tip of the microscope, it is possible to visualize individual atoms and the structure of individual molecules.



“It was only by using this Raman sensor that we were finally able to demonstrate the molecular switching process.”

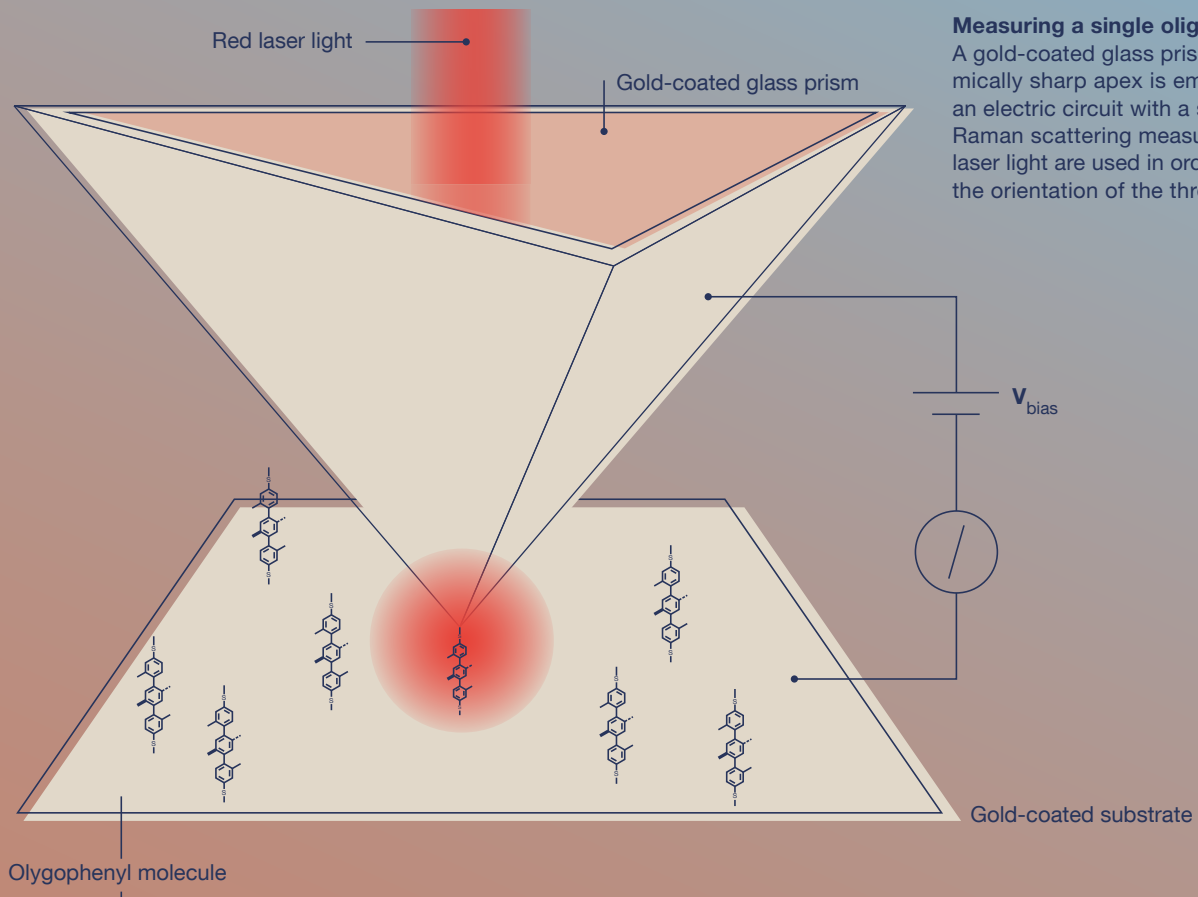
Joachim Reichert

A look inside the measurement chamber: A gold-coated glass prism is used to electrically connect an oligophenyl molecular switch.

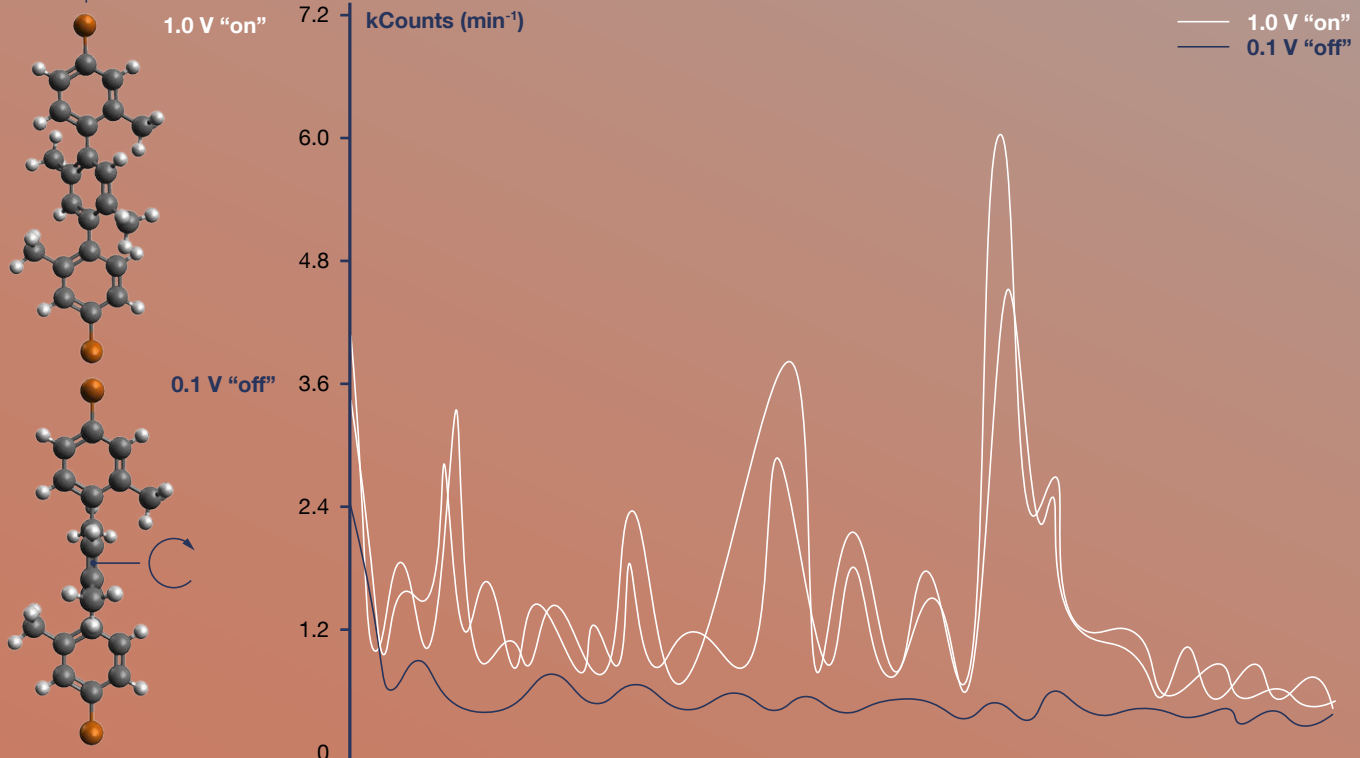
Picture credits: Astrid Eckert/TUM

Atomic force microscopes probe samples physically. The forces exerted on the tip alter the frequency of oscillation of a tiny cantilever in the microscope. By measuring these changes in frequency, it is possible to produce images with atomic resolution. “We can also use this technique to stimulate and modify the molecule,” says Auwärter. In addition, by combining the two methods, he has been able to characterize chemical bonds and even determine the charge distribution in a metal-organic complex made up of cobalt and a phthalocyanine scaffold. This is an important step in understanding the electronic properties of this compound.

These measurements are made easier by using a special substrate for the molecular probes. Auwärter did not use pure monocrystalline gold or iridium substrates. Instead, he used a copper substrate, which he coated with an atomically thin layer of boron nitride. Because boron nitride acts as an electrical insulator, his sample was electrically decoupled from the substrate. Using this method, Auwärter and his team were able to measure the electronic properties of molecules and molecular aggregates in the absence of distorting interactions with the metal substrate. ▷



Measuring a single oligophenyl switch. A gold-coated glass prism with an atomically sharp apex is employed to create an electric circuit with a single molecule. Raman scattering measurements with red laser light are used in order to determine the orientation of the three phenyl rings.



The olygophenyl molecule switches when all three phenyl rings adopt a coplanar orientation.

A controlled fragmentation process produces glass prisms with an atomically sharp apex.

Picture credits: Astrid Eckert/TUM; Graphics: ediundsepp (source: TUM/Joachim Reichert)

Electrodes for individual molecules

Auwärter is gradually refining his scanning probe microscopy techniques to enable analysis of individual functional molecules. In parallel with this, Joachim Reichert is expanding the palette of molecular engineering techniques available to the Munich team by developing a clever new tool. With this new approach it became possible to scrutinize an individual oligophenyl switch. The challenge was to create an electrical circuit using a single molecule. Reichert used glass that had been subjected to a controlled fragmentation process to produce an atomically sharp apex. Coating the glass with a ultra-thin layer of gold produces an extremely sharp electrode tip, using which the oligophenyl molecule can be connected to a counter electrode. And it gets better: through the glass, Reichert shone red laser light, which was scattered by the switchable molecular species. This is known as Raman scattering, and by measuring it the researchers were able to obtain data on the chemical structure of the molecule at different applied voltages. “It was only by using this Raman sensor that we were finally able to demonstrate the molecular switching process,” explains Reichert.

“Our research unit brings together the ability to prepare functional elements at the molecular level with the methods needed to analyze them,” explains Johannes Barth. The spectrum ranges from molecular switches and photoactive molecules to tiny carbon nanowires and magnetically active systems. Each new approach, each new material, each experiment gives Barth and his 30 or so colleagues a further insight into the versatility of and exciting opportunities offered by molecular engineering. “We are laying foundations that could lead to real applications in areas ranging from nanoelectronics to photonics to catalysis.”

Jan Oliver Löfken