Pinning **Molecules Down**

Wilhelm H. Auwärter successfully investigates single molecules and the way they work by attaching them to tailored surfaces and examining them with a scanning tunneling microscope.

Picture credit: Jooss

Brigitte Röthlein

Moleküle unter Beobachtung

Ganz ohne Zwang, nur durch Selbstorganisation, bilden sich unter bestimmten Bedingungen Schichten aus Bornitrid, die nur eine Atomlage dick sind. Der Liechtensteiner und Schweizer Physiker Wilhelm H. Auwärter und sein Team stellen solche Schichten in den unterschiedlichsten Variationen her und benutzen sie dazu, Moleküle, die sich darauf festsetzen, mit dem Rastertunnelmikroskop abzutasten. Dies gibt ihnen die Möglichkeit, die Moleküle und ihr Verhalten auf atomarer Ebene zu untersuchen.
Im Vordergrund stehen dabei Porphyrine, organische Komplexe, die ein Metallion enthalten. Ihre chemische Struktur besteht aus vier Ringen, die zyklisch miteinander verbunden sind. Im Zentrum sitzt das Metallion. In ihren verschiedenen Ausprägungen spielen Porphyrine beispielsweise im menschlichen Stoffwechsel eine zentrale Rolle. So sorgen sie für den Transport des Blutsauerstoffs im Hämoglobin und kommen in vielen Enzymen vor. Sie zeigen ihre Wirkung aber auch im Chlorophyll, wo sie entscheidend an der Photosynthese beteiligt sind.
Die TUM Forscher fixieren diese Moleküle im Vakuum und bei tiefen Temperaturen auf der Bornitridschicht und setzen sie unterschiedlichen Bedingungen aus. Mit Hilfe des Rastertunnelmikroskops können sie dann beobachten, wie sich die Struktur der Moleküle verändert, welche Verbindungen sie eingehen und welche Varianten für bestimmte Zwecke besonders gut geeignet sind.
Mit diesem Verfahren lässt sich eine Vielzahl organischer und anderer Moleküle beobachten. Die Erkenntnisse helfen dabei, elektrische, magnetische und optoelektronische Eigenschaften von Materie zu optimieren. Anwendungen sind denkbar für organische Solarzellen, für reversible molekulare Schalter, für Sensoren oder neuartige Katalysatoren. Aufgrund der großen Bedeutung seiner Arbeiten erhielt Auwärter im vergangenen Jahr für seinen Projektvorschlag mit dem Namen NanoSurfs von der EU einen ERC Consolidator Grant, der mit knapp zwei Millionen Euro dotiert ist und seine Arbeit bis 2019 fördert. □

Link
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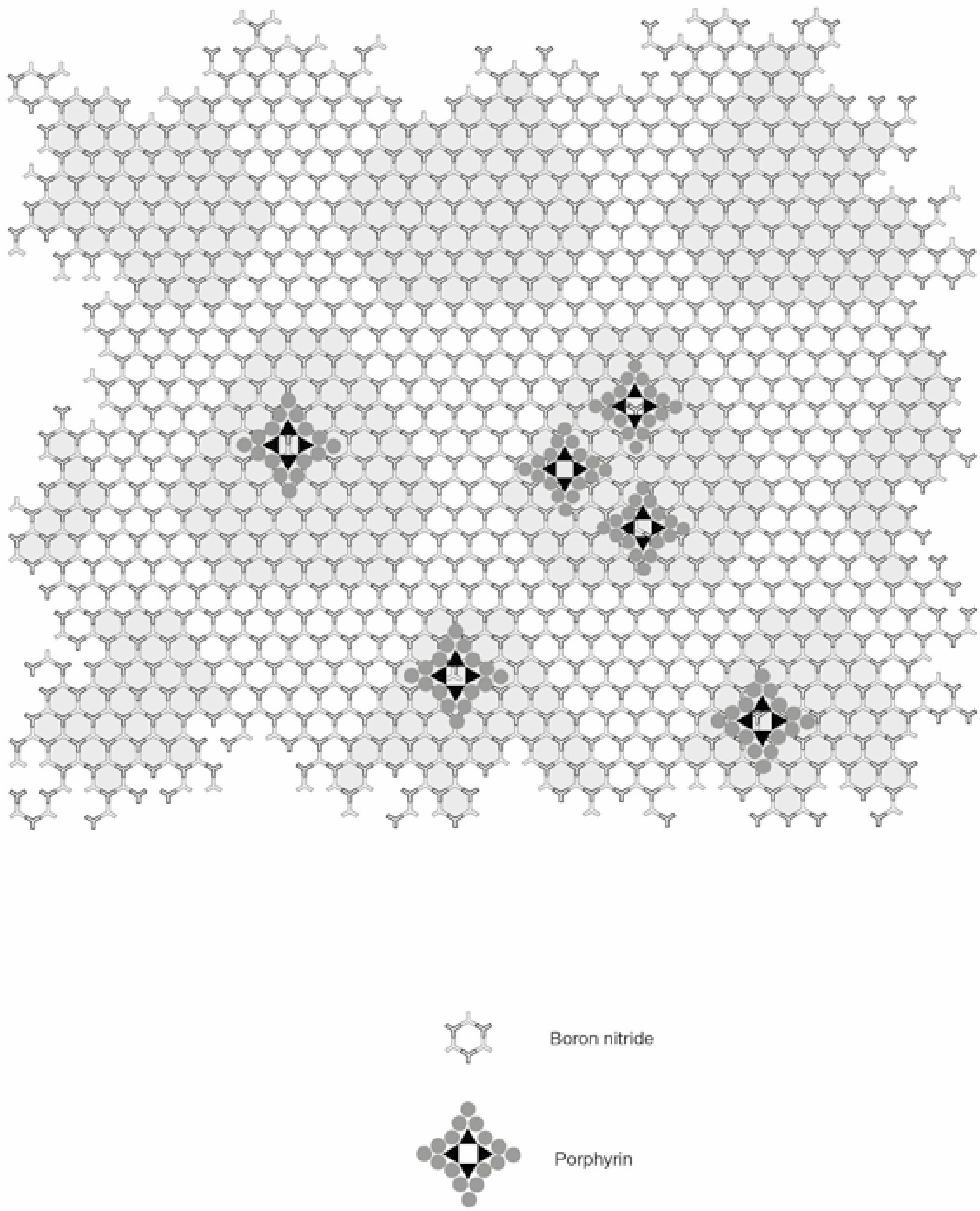
Insect researchers like to study their subjects by fixing them with pins and observing them at leisure. Wilhelm H. Auwärter does much the same thing with molecules – except that molecules are way smaller and remain "alive". Which is the whole point of the experiment, in fact, as he is looking to observe the way they behave and perform various functions. And instead of pins, he uses the natural properties of the molecules to fasten them to a substrate.
The work of physics professor Auwärter at TUM is closing a gap in the study of organic molecules. Analytical methods exist to determine their chemical composition; X-rays can be used to establish their physical structure; and chemical analyses can test their activity patterns. All of that contributes to our current conceptual understanding of particular molecules. But nobody had ever really seen them before, because they are simply too small for optical microscopes. Now, though, Auwärter and his team are making these tiny structures and their functionality visible.

Growing layers one atom thin

In recognition of the importance of his efforts, Auwärter was awarded an ERC Consolidator Grant by the EU last year for his NanoSurfs project proposal. With funding of almost two million euros, the grant will support his research until 2019. "This is a tremendous boost to our efforts," confirms the delighted scientist. "It means we can focus fully on our work and also acquire an atomic force microscope to supplement our analyses."
At the heart of Auwärter's work are ultrathin layers of boron nitride, vapor-deposited onto a base material, which is ▷



Picture credit: ediundsepp (Source TUM)

How to pin a molecule down (schematic illustration): Auwärter and his team grow ultrathin layers of boron nitride, which forms a honeycomb lattice much like graphene. Onto this substrate, they sublimate metalloporphyrin molecules, which attach themselves lightly to the boron nitride layer. With the help of a scanning tunneling microscope, one can then observe how these molecules behave, for instance when a gas molecule is in the vicinity.

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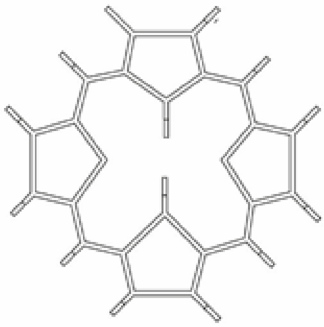
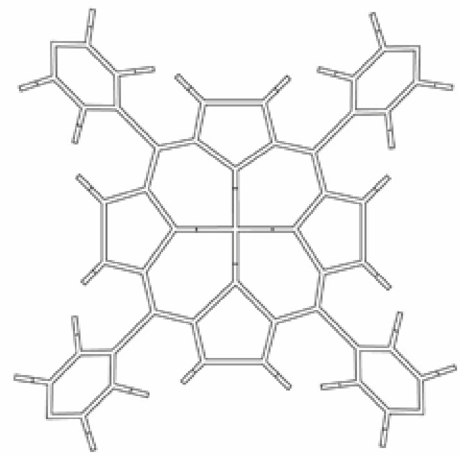
Wilhelm H. Auwärter

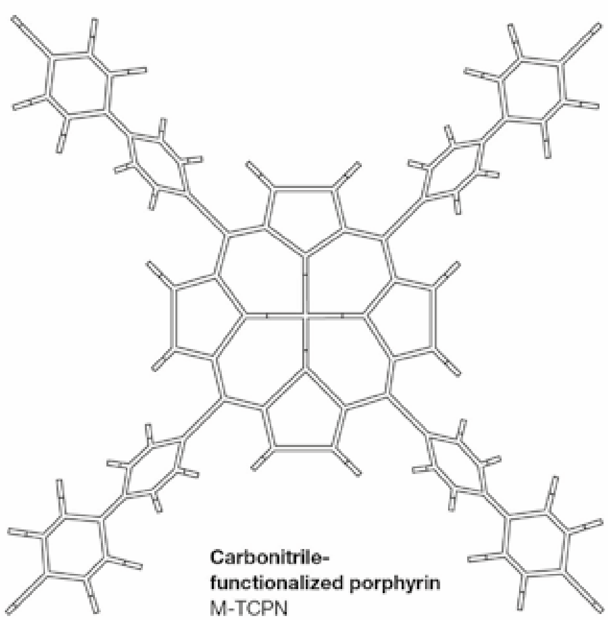
Picture credit: Jooss



Porphine
2H-P
free-base porphine



Tetraphenylporphyrin
M-TPP
metallotetraphenylporphyrin



Carbonitrile-functionalized porphyrin
M-TCPN
metallotetra
[(4-cyanophenyl)-phen-4-yl]
porphyrin

Three of the porphyrin molecules Auwärter works with. Porphyrins in their various forms play a key role in human metabolism, for instance, or in photosynthesis.

Picture credit: ediundsepp (Source: TUM)

usually metallic. The process entails placing single crystals of the metal in a vacuum chamber, inside which a precursor substance containing boron and nitrogen is then evaporated. If this is done correctly, the resulting vapor settles on the monocrystal in a layer just one atom thin. The boron and nitrogen atoms are then compelled to arrange themselves in a certain way on the substrate and adopt a specific configuration. "This is a special property of boron nitride – and actually of graphene too," explains Auwärter. "As a rule, the layer can only spread out in two dimensions, so has no bulk."
The atomic structure of this lattice is revealed with a scanning tunneling microscope (STM). This device – "a cool invention" by subsequent Nobel Prize winners Gerd Binnig and Heinrich Rohrer – is capable of imaging surfaces so precisely that every single atom can be seen. Used to analyze the boron nitride layer, the STM reveals the formation of a flat, honeycomb lattice. By now, Auwärter and his team have become experts at producing this type of lattice in a wide range of variants. Nickel is most commonly used as the metallic base, but if this is substituted with rhodium, the two crystal structures do not overlap exactly and regular wrinkles form where the layer is slightly elevated. Other tricks can be used to produce wave and step effects or modify the electronic structure. The researchers are even attempting to insert other atoms or molecules between the base material and the boron nitride layer, with examples including silver and graphene.

"These molecules are so important that it is essential for us to understand exactly how they function on surfaces. Only then can we fully harness their technical potential."

Wilhelm H. Auwärter

Observing the behavior of metalloporphyrins

Onto this prepared substrate, Auwärter and his team then vaporize molecules such as metalloporphyrins. These are organic complexes containing a metal ion. Their chemical structure consists of four cyclically linked rings with the metal ion at the center. Porphyrins in their various forms play a key role in human metabolism, for instance. They enable hemoglobin in red blood cells to carry oxygen and also occur in many enzymes. They can be found in chlorophyll, where they make a key contribution to photosynthesis. "These molecules are so important that it is essential for us to understand exactly how they function on surfaces. Only then can we fully harness their technical potential," emphasizes Auwärter. Which is why he is attaching them to the boron nitride lattice in a high vacuum and usually at extremely low temperatures. He then observes how they behave as soon as a gas atom is in the vicinity. Since the molecules are placed lightly on the substrate, they can still move. And sometimes they also change structure, break up or bind with other molecules.
The primary tool for these observations is a scanning tunneling microscope, with an atomic force microscope planned as a future addition. At the core of the STM is a probe, consisting of an extremely fine tungsten needle, ideally with a point comprising a single atom. This is guided at close range across the surface whose atoms are to be examined. If the needle tip is directly above an atom on the surface, at a distance of approximately one nanometer, every now and then an electron will tunnel between the needle and the surface. A current, though miniscule, will flow – known as the tunnel current. If the probe systematically scans the surface and records the strength of the tunnel current at each point, it yields an image of that surface that is so precise it even shows the elevation of individual atoms. "We can see how the molecules cluster on the patterned boron nitride, for ▷


VAT

Prof. Wilhelm Auwärter

From Zurich to Munich – via Vancouver

Doing the right thing at the right time can make a science career. In Wilhelm H. Auwärter's case, things seemed to fall into place automatically, although it is only now, many years on, that he sees it that way. "It was really all coincidental," remarks the 41-year-old Liechtenstein citizen and Swiss passport holder, now a Heisenberg Professor at TUM. "I used a scanning tunneling microscope to analyze boron nitride layers for my degree thesis in Zurich in 1998, but it didn't arouse all that much interest back then." It was only years later when graphene was discovered – which has an almost identical geometrical structure – and a Nobel Prize was awarded for that discovery, that Auwärter's findings began to interest many colleagues, leading to frequent citations of his earlier publications.

In the meantime, he continued pursuing the topic for his doctorate and developed his expertise in producing boron nitride layers and analyzing them with a scanning tunneling microscope. As a postdoc, he relocated to Vancouver due to the outstanding research framework on offer there. He and his wife remain very fond of that beautiful city surrounded by mountains and sea and still sometimes feel a bit homesick for it. "Maybe it will work out so that we can live there again, at least for a while," he hopes. Although, back in the day, it was no mean feat convincing his girlfriend (now wife) to give up her job in Zurich and go with him to Canada in the first place.

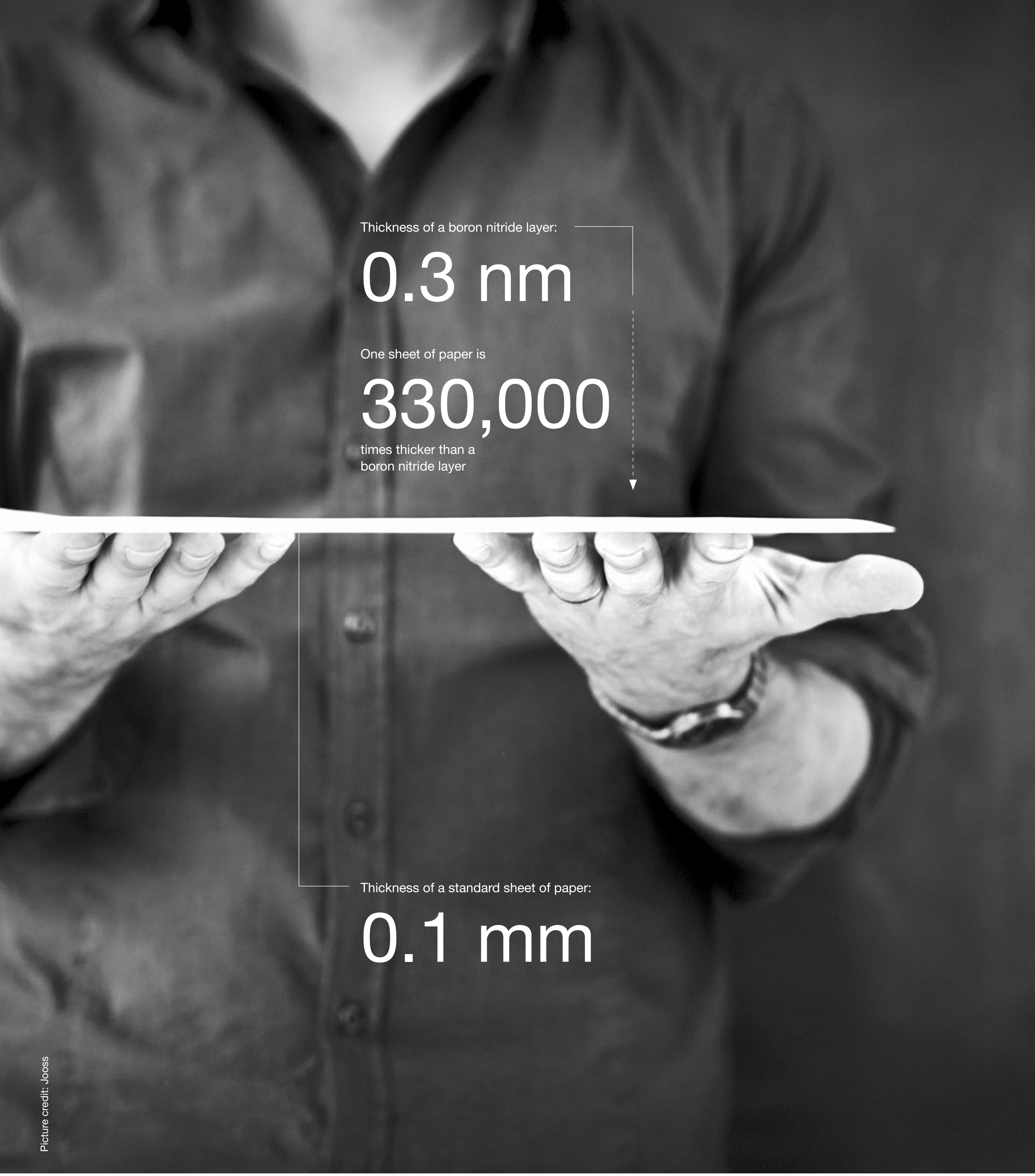
Now married, they have two children, aged three and five, who see visiting their dad at the university as a special treat: "They're delighted by the huge chalkboard and colored chalks in the seminar room and love it if they're allowed to pick up a wrench, since that's a grown-up tool."
In fact, a university career was not always Auwärter's aim – he could see himself working as a school teacher too. And although it turned out differently, he still enjoys teaching and does all he can to interest students in his physics lectures.

Picture credits: Jooss

instance," describes Auwärter, adding, "Or we can determine which bonds our molecules form; how their 'feelers' interact with their neighbors." By conducting a tiny current through the tip of the microscope, the researchers can even induce vibration in the atomic structures and thus learn more about their structure.
At the moment, of course, all this is purely basic research – but with a real prospect of important applications in the long term. "Producing synthetic catalysts might be a possibility, for instance – that is, molecules that have the effect of provoking a specific chemical reaction," Auwärter reflects.

Atomic switches for extremely small sensors
As a concrete practical example, the TUM scientists are currently working with colleagues in Berkeley, California, to research processes inside novel organic solar cells. The aim is an atomic-scale investigation of the changes organic molecules in these solar cells undergo when irradiated with photons and how they transfer the released electrons to other molecules. Only when this information is established in detail will it be possible to set about optimizing the solar cell chemistry – similar to tiny Lego bricks you can use to build and modify the shapes you need. "This type of information is significant because, if we want to find molecules that are particularly fit for purpose, we need to know beforehand how they are oriented and coupled," Auwärter points out.
Another application for this method is atomic switches, created under specific conditions when molecules modify their structure – such as reorienting a bond – and thus suddenly change properties. Such reversible switches would be ideal for use in extremely small sensors.
Auwärter is well aware of the numerous possibilities open to him and his research team. However, he has made a deliberate decision to focus on his core competency, i. e. the study of molecules on suitable substrates like boron nitride. To achieve this, his team works in close collaboration with theoretical scientists, who interpret the results from a quantum-mechanical viewpoint and support them with simulations. "As labor-intensive as the ERC grant application was, it did give me a chance to consider where I've got to and what I want to achieve," says the physicist. "The hectic pace of day-to-day research means you never usually get the opportunity to take stock that way." When it comes to future research objectives, his plans are far-reaching, the aim being to create new ways of optimizing electric, magnetic and optoelectronic material properties at molecular level. The knowledge and hands-on experience Auwärter has gathered during his years of work in this field are surely unparalleled and will stand him in good stead in pursuing his goals. Even now, as a professor, he likes to spend a few hours here and there optimizing the microscope's scanning tips and imaging newly prepared surfaces. "You need experience and a good feel for what you're doing," he concludes. "And sometimes you just do something by intuition and couldn't really explain exactly why."

Brigitte Röthlein



Just one atom thin are the boron nitride layers Wilhelm Auwärter produces in his lab. He and his team can even grow a wide range of variants of these layers, producing certain structures that allow them to capture molecules on the layer surfaces and study their behavior.