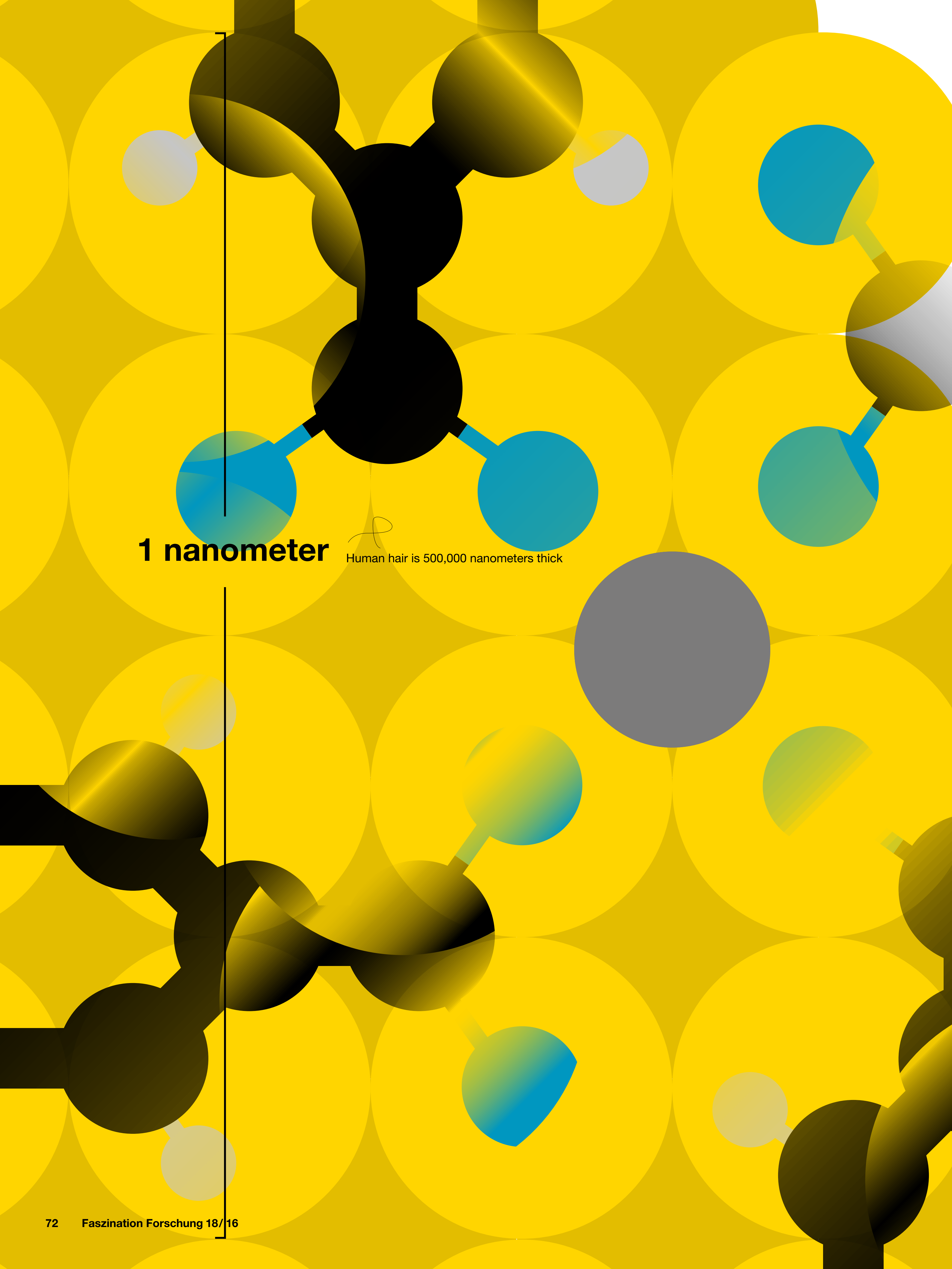


1 nanometer

Human hair is 500,000 nanometers thick

Magically Drawn to the Interface

Johannes Barth likes to research at the edge. He is interested in harnessing the properties of complex single molecules and creating nano-scale architectures with useful functionalities. The research of his team is laying the groundwork for novel kinds of materials and processes in molecular nanoscience and technology.

Graphics: ediundsepp (source: TUM)

Link

www.e20.ph.tum.de

Gerlinde Felix

Grenzflächen als magische Spielwiese

Molekulare Nanostrukturen sowie winzige Funktionseinheiten auf Grenzflächen stehen im Mittelpunkt der interdisziplinären Grundlagenforschung des Physikers Prof. Johannes Barth und seiner Mitarbeiter. Barth und sein Team suchen insbesondere innovative Ansätze, um gezielt funktionelle Nanosysteme aufzubauen. Diese ebnen die Grundlagen für innovative Konzepte im Bereich der Nanomaterialien, Nanoelektronik, Photonik und Spintronik – um einige der möglichen Anwendungsbereiche zu nennen. Die Wissenschaftler nutzen für die Herstellung von Nanostrukturen ein Prinzip, das sie sich von der Natur abgeschaut haben: Die Selbstassemblierung, die auf der Erkennung und auf gerichteten Wechselwirkungen zwischen den einzelnen Akteuren beruht. Die Natur erzeugt dadurch biologische Gebilde wie Zellmembranen, Zellfabriken und die DNS. Dafür bedarf es keines Baumeisters, keines Plans und keines Gerüsts, denn die Strukturelemente tragen ihre Bestimmung schon in sich. Ähnliche Vorgänge laufen in Barths Labor ab, wenn sich beispielsweise Metallatome und maßgeschneiderte organische Moleküle auf einem geeigneten Substrat zu metall-organischen Nanostrukturen zusammenfinden. Die Kunst dabei ist, die richtigen Komponenten mit abgestimmten Funktionalitäten auszuwählen, um die Wechselwirkungen, die zur Selbstassemblierung führen, gezielt zu nutzen. Barths Forschung geht aber noch weitere Schritte. So entstehen in den Münchner Labors beispielweise honigwabenförmige Nanonetzwerke mit kleinen Rotoren, Quasikristalle, Nanosolarzellen und molekulare Drähte. Insbesondere die Forschung zu sich selbstassemblierenden Nanostrukturen wurde dank eines European Research Council Grants, den Barth 2009 für sein Projekt MolArt – Surface-Confined Metallosupramolecular Architecture erhielt, möglich. Barth, der seit bald vier Jahren auch Dekan ist, schreibt dem ERC einen Booster-Effekt für seine Forschungsaktivitäten im Bereich der Nanowissenschaften und für die Förderung von Nachwuchswissenschaftlern zu. Dass seine administrative Arbeit mit Wissensgewinn vereinbar ist, sei, so der Physiker, innovativen Ideen, einem guten Stamm an Mitarbeitern und synergetischen Kooperationen, beispielsweise auch mit Partnern am Zentralinstitut für Katalyseforschung und im Exzellenzcluster Munich Center of Advanced Photonics, zu verdanken. ☐

Prof. Johannes Barth

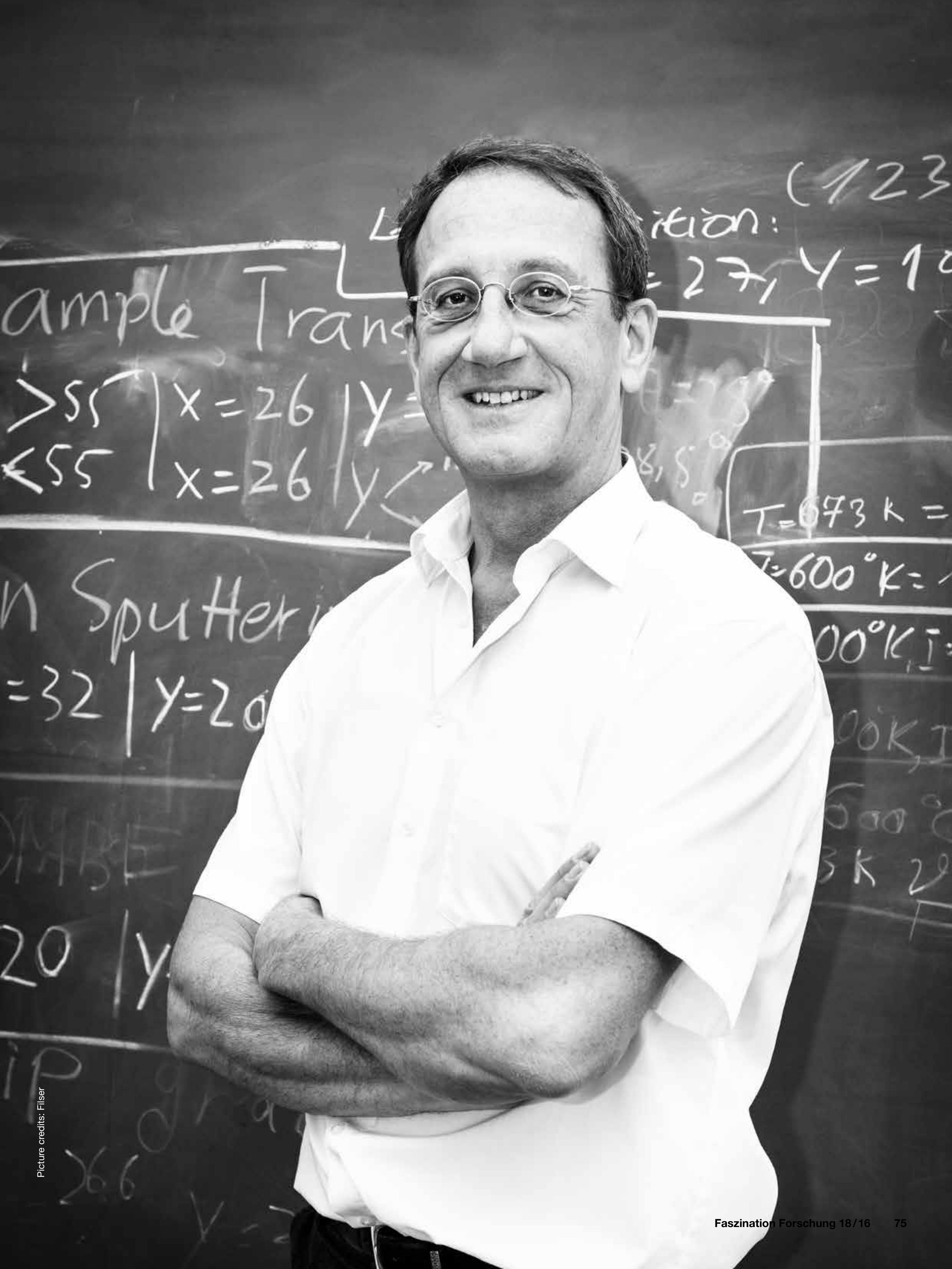
Always at the interface

After toying with the idea of studying music or humanities, Johannes Barth eventually decided on physics, guided by his fascination with quantum mechanics. He was tempted by medicine along the way, but neurophysiology simply did not have a strong enough fundamental physics element. In 1988, he focused on his diploma thesis, which was half experimental and half theoretical, in Munich and Berlin at the Fritz Haber Institute of the Max Planck Society. So he experienced the special atmosphere – and all the restrictions – that defined Berlin before the wall came down. In 1989, he nonetheless moved to Berlin and the Fritz Haber Institute. There he received his doctorate in physical chemistry, specializing in surface studies, with Prof. Gerhard Ertl, who went on to win the Nobel Prize in Chemistry. He was in Berlin to witness the historic events surrounding the fall of the wall. “Previously, the S-Bahn only went as far as Friedrichstraße, but suddenly it just kept going. Those were amazing times.”

After obtaining his doctorate in 1992, he moved to the IBM Almaden Research Center in San Jose, USA where he spent 18 months as an IBM Postdoctoral Fellow and Humboldt scholar. His research there focused on ultrathin magnetic films for storage technology. IBM went through a financial crisis at the time and had to close several labs, so Barth attended a large number of farewell parties, besides benefitting from the stimulating scientific environment and life in California. After that he returned to Berlin before moving on to the École Polytechnique Fédérale de Lausanne in Switzerland. He dedicated all his research efforts there to interface chemistry, transport processes of adsorbates and growth of thin films. He later went on to work with organic molecules and focused his experimental efforts on supramolecular structures and metal-organic architectures. He received his lecturing qualification (venia legendi) in 1999. After spending more than ten years in Lausanne, and having climbed a series of 4,000 m peaks in the Alps, he accepted an offer as Canada Research Chair from the University of British Columbia, Vancouver, in 2003. While rapidly installing a successful lab, he was also able to enjoy sushi, beach barbecues, jogging by the Pacific and powder snow in the nearby ski resort of Whistler.

In 2007, he moved to TUM as a full professor while remaining an adjunct professor at UBC Vancouver for a few more years. Barth has had a large number of papers with high impact published in renowned scientific journals. In 2009, he received the ERC Advanced Investigator Grant for his “MolArt – Surface-Confined Metallosupramolecular Architecture” project. The ERC grant provided the creative headroom and extra manpower needed to bring his research to the next level. Four years ago, Barth was appointed Dean of the Physics Department.

> *“Our basic research represents a starting point for the development of new materials and concepts. Looking beyond molecular electronic components, spintronics, solar cells and IT building blocks, we are also thinking designer catalysts.”*
>
> *Johannes Barth*



Picture credits: Filser

Welcome to the nanocosmos, a world where structures are measured in billionths of a meter. These could be aggregates of atoms, ultra-precise magnetic and semiconductor elements, or likewise a virus, the bacterial ribosome in which the gut bacterium *Escherichia coli* creates its proteins, or even the double helix of a DNA molecule. At first glance, the latter biological structures have very little in common with the research of Prof. Johannes Barth, Chair of Molecular Nanoscience & Chemical Physics of Interfaces. But a closer look shows a different picture. The physicist, who is also Dean of TUM's Physics Department, and his team base their work around a scenario devised by evolution long ago: the principle of self-assembly. Without this principle, there would be no life on earth. It facilitates energy-optimized

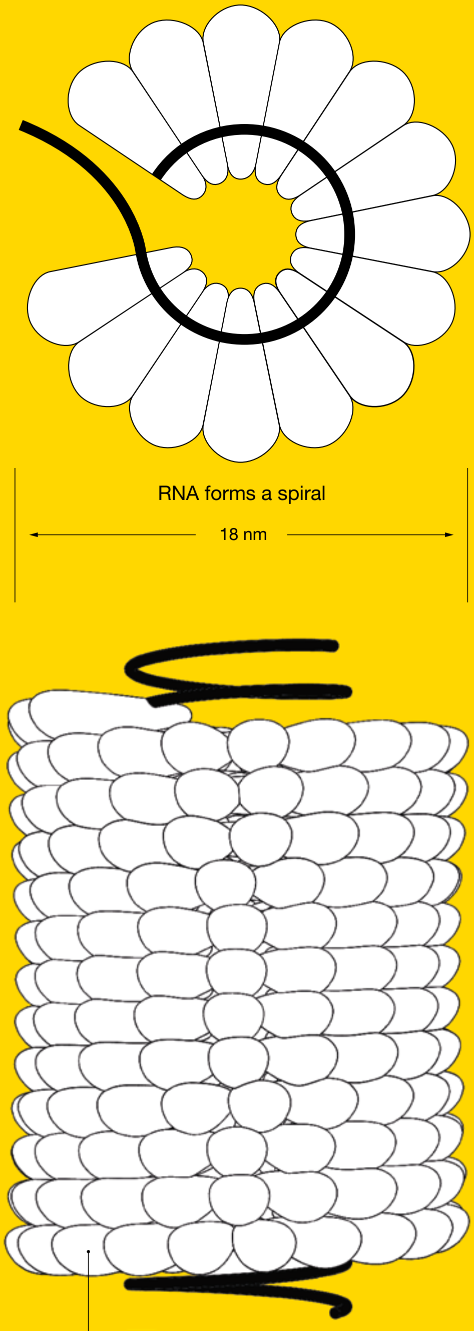
Thanks to the ERC project MolArt, Johannes Barth's research group now operates this scanning tunneling microscope combined with an electrospray ionization scanning setup. It is designed to handle complex and thermolabile species for nanoscale investigations.

structures spontaneously evolving from basic constituents that themselves originate from chemical reactions. Their spatial arrangement, that is, the formation of ordered, typically highly organized structures, results from the subtle interplay of "weak" intermolecular forces. "The phenomenon of self-assembly is incredibly fascinating and multi-faceted," enthuses Barth, who has a certain weakness for biophysical chemistry and is now conducting interdisciplinaary research embracing physics, nanoscience and supramolecular chemistry. In 2009, he received a EUR 2.6 million grant from the European Research Council (ERC) for his "MolArt – Surface-Confined Metallosupramolecular Architecture" project. This grant paved the way for a number of basic research projects on self-assembled nanostructures; the success of which – according to Barth – was attributable to excellent working conditions, a wealth of ideas and the high commitment of the researchers. Several projects brought TUM's physicists and chemistry departments together with scientists from Karlsruhe, Linköping, Lyon, Namur, Paris and Zurich. Quite a few endeavors left the realm of self-assembly, including very challenging experiments with individual molecules. It is possible that major technical applications will be found for the molecular functional architectures created by Barth and his team. "Our basic research represents a starting point for the development of new materials and concepts. Looking beyond molecular electronic components, spintronics, solar cells and IT building blocks, we are also thinking designer catalysts," says Barth. This echoes the words spoken many years ago by eminent physicist Richard Feynman, who asserted that the control of matter at atomic level could open up a huge number of new applications: "When we get to the very, very small world we have a lot of new things that represent completely new opportunities for design … We will get an enormously greater range of possible properties that substances can have, and of different things that we can do … We can manufacture in different ways."

Emulating natural processes

So what "recipe" are the researchers following to realize self-assembled functional architectures? The key to their design is a selection of the right building blocks with programmed properties that are brought together under suitable conditions. Self-assembly on the nanoscale makes use of intermolecular interactions – just like nature, where molecular recognition also plays a crucial role. These interactions include hydrogen or van der Waals bonding, the electrostatic forces between charged particles, and metal-ligand interactions (combining metal atoms and molecules). With the help of thermal energy and these "weak" forces, the players "push

Picture credits: Filser, Graphics: ediundsepp (source: TUM)



About 2,130 protein units assemble themselves along the RNA to form the tabacco mosaic virus.

Nature employs self-assembly to form stable structures such as viruses. Protein subunits are organized around a single strand of RNA to form a stable structure capable of self-replication.

and shove" until they arrive at their optimum position. Unlike chemical reactions, atomic bonds are typically not formed. In order to produce surface-confined metal-organic or other hybrid systems, the first step involves selecting a suitable substrate. This can be a regular grid of silver, gold or carbon atoms, for example. Importantly, the geometric and electronic structure of a metal lattice influences the processes that take place thereon and the properties of the evolving structures. Accordingly the surface – acting as a "design platform" – must be atomistically clean and well-defined. Any imperfections could hinder the movement and association of the atoms or molecules. The physicists thus have to lend a "helping hand" and first prepare the surface. "Optimum interfaces are not always easy to achieve. But after extensive practice we have the necessary expertise," says Barth.

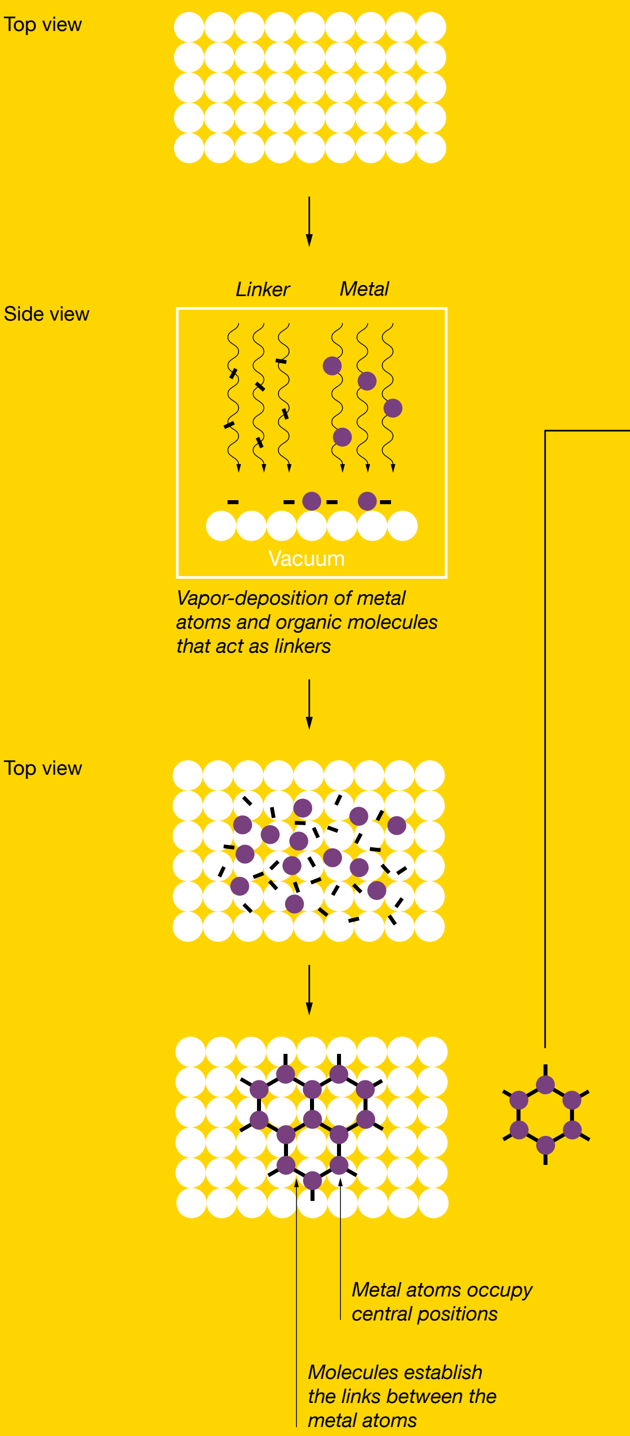
How nanostructures are formed

The substrate is "only" the base layer, however. In order to create metal-organic nanostructures, the researchers vapor-deposit selected organic molecules (so-called linkers) followed by metal atoms (such as iron) under vacuum conditions. Once all the players are in place, they reassemble into new one- or two-dimensional structures as if by magic. During self-assembly, the organic molecules are linked to the metal atoms, which occupy central positions in the resulting structures. In fact, through their properties, they steer the self-assembly process. Suitable metal candidates include iron and cobalt, both magnetic elements, then cerium or europium, which are rare earths (lanthanides), as well as catalytically active transition metals like rhenium, tantalum, tungsten, vanadium and chromium. With these metals, only a small amount of energy is required to detach valence electrons. For reasons related to quantum mechanics, an atomic magnetic moment may additionally arise which could also be important for targeted functionalities and for the interplay between metal atoms, substrate and linkers. Suitable organic molecules include biologically important tetrapyrrole rings, carboxylic acids and de novo synthesized linear polyphenylene-dicarbonitrile molecules. These building blocks may have complicated, tongue-twisting names but – and this is the crucial ingredient – their end groups and backbone have suitable characteristics. Thus a rich variety of structures is produced. These may be individual metal-organic complexes such as a macrocycle with a metal atom at its center. Or they include one-dimensional chains or regular two-dimensional metal-organic coordination networks, which may even act as seed layers for 3D structures. Depending on the properties of a given structure, possible future applications include new nanomaterials, molecular electronics, organic solar cells, molecular magnetism, new catalysts and biosensors.

Importance of scanning probe microscopy

Barth's basic research into interface phenomena and nanostructures would hardly be feasible without a special tool: ▷

How to produce self-assembled functional structures at interfaces



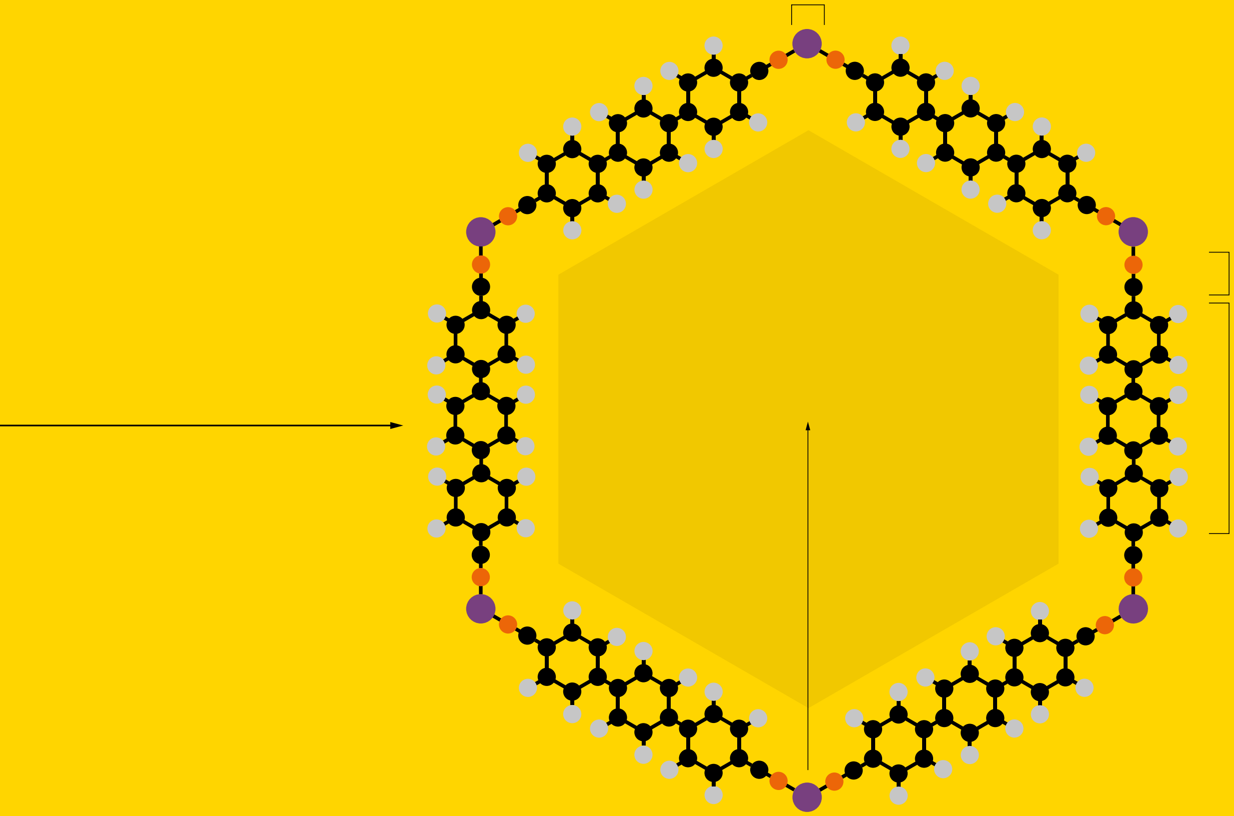
Vapor-deposition of metal atoms and organic molecules that act as linkers

Metal atoms occupy central positions

Molecules establish the links between the metal atoms

Graphics: ediundsepp (source: TUM)

Correlation between structure and functionality



Metal centers account for
- *electronic structure*
- *magnetic properties*
- *chemical function*

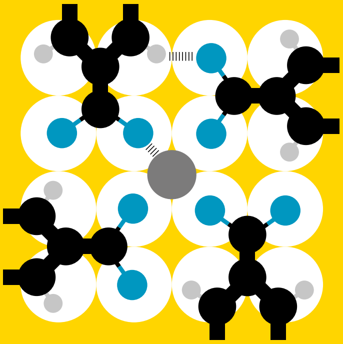
Ligand controls
- *lateral linkage*
- *metal center position*
- *overall functionality*

Linker backbone provides
- *network structure*
- *rim functionality*
- *photonic and other features*

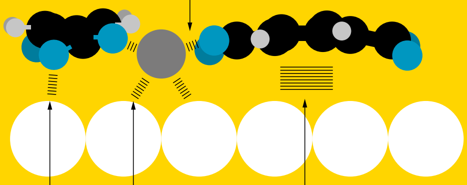
Nanocavity affords space for
- *templating or caging*
- *selective sorption*
- *nanoreactor*

Forces behind self-assembly in 2D

Top view



Side view



Metal-ligand interaction

van der Waals bonding

Metal-substrate interaction

Linker-surface interaction

○ Substrate
● Hydrogen
● Oxygen
● Nitrogen
● Carbon
● Iron
● Cobalt
|||||| Stabilizing forces

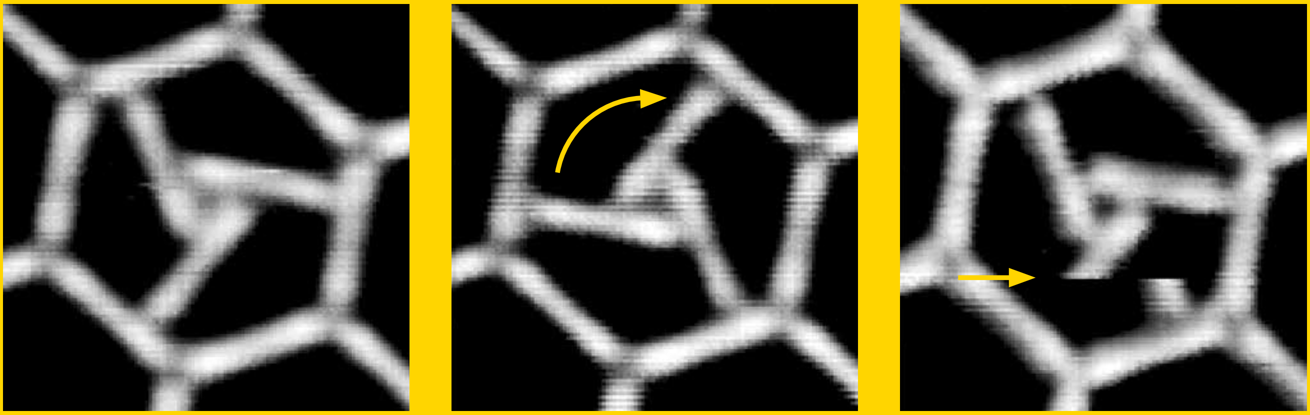
This combined scanning tunneling and scanning force microscope is used by the researchers to investigate molecular features and functionalities in unprecedented detail.

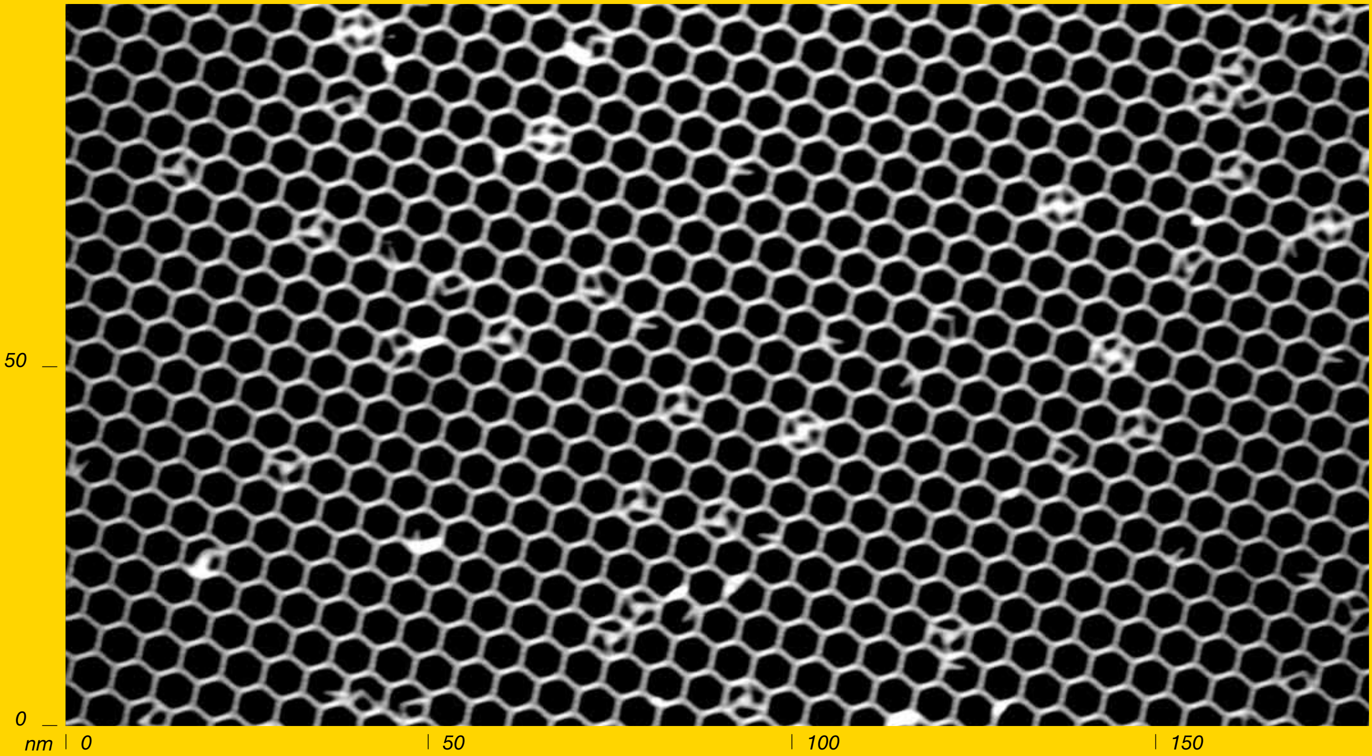
the scanning tunneling microscope (STM). This microscope scans the surface with the overlying structure and measures the local density distribution of the electrons. It allows the researchers to track what happens at the atomic level if one of the players undergoes a change. “In this way, we can follow structure formations and dynamics with molecular- or even atomic-level precision. The scanning tunneling microscope along with other techniques provides a rounded picture,” says Barth. The team can also track the nature of diffusion processes on a surface. Other methods, such as X-ray photoemission spectroscopy or computer-aided (simulation) models, are used to investigate the resulting structures and their properties. X-ray absorption spectroscopy provides complementary information on the chemical composition, geometry or magnetic features. Computer-aided simulation models reveal the bond characteristics and the nature of the underlying processes and driving forces.

The inner workings of a honeycomb

What are two-dimensional, metal-organic coordination networks exactly? Well, they can be created, for example, when cobalt atoms and rod-like organic molecules acting as connectors are vapor-deposited consecutively onto a silver substrate. Then they form a strikingly regular “honeycomb” structure no more than one atomic layer thick. This is a network of many, side-by-side hexagonal cells only a few square nanometers in size. The cobalt atoms define the six corners of the cell and the organic molecules the rims. The fact that a network of hexagonal cells is formed rather than simple chains is down to the fact that the cobalt atoms prefer to “bond” at the corners of the cells in three directions. The researchers varied the length of the linkers and observed what happened. Together with their cooperation partners from the Karlsruhe Institute of Technology, they discovered that the size of the cells or pores (e.g. 24 nm^2) can be systematically adjusted through the length of rod-like organic molecules. The players repair any faults in the network themselves. So what happens when the network is fully developed and additional “rodlets” are vapor-deposited? The answer is something astonishing, which also took the TUM researchers by surprise. Three small rodlets tend to accumulate in certain cells of the honeycomb, while other cells remain empty. It seems that it is more energy-efficient to gather in one cell as a threesome than for each to occupy its own cell. Highly detailed observations with the scanning tunneling microscope reveal why this is so. The three rod-like molecules arrange themselves in this way because they can form a node while their ends simultaneously interact with the edge of the pore. Viewed from ▷

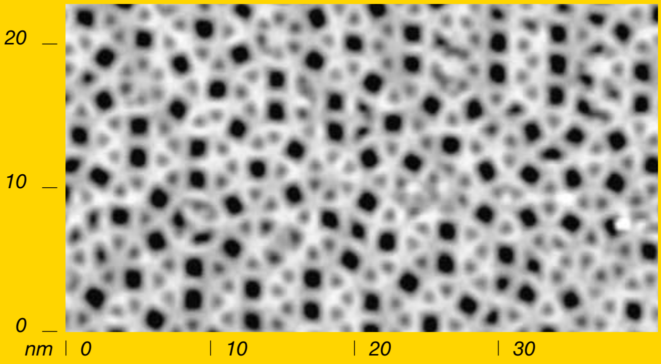
Picture credits: Filser, TUM

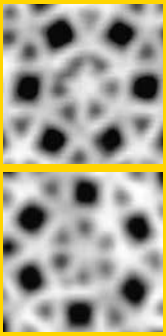


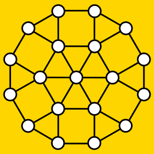


⬡ 24 nm^2

Cobalt atoms and rod-like organic molecules (see page 79) form a “honeycomb” nanomesh no more than one atomic layer thick when deposited onto a silver substrate. If additional “rodlets” are vapor-deposited onto a fully developed network they assemble in certain cells of the honeycomb, forming a three-blade rotor whose movement the physicists can control by adjusting the temperature. The above images show the rotation at a temperature of 64 kelvin, 204 seconds elapsed between subsequent stages.







The influence of the metal atom on the nanostructure. While cobalt atoms and organic molecules called cyano-linkers yield a “honeycomb” nanomesh (top), replacing cobalt with europium leads to a radically different structure with quasi-crystalline order characteristics.

> *“The phenomenon of self-assembly is incredibly fascinating and multifaceted.”*
>
> *Johannes Barth*

above through the STM, the pattern looks like a three-blade rotor. This arrangement of the molecules is so robust that additional energy in the form of temperature increase does not cause the trio to disintegrate. “This movement is not a rotation in the usual sense, but rather a sequence of transitions between four different states.” By turning the temperature knob, the TUM researchers were able to determine the energy threshold at which the dynamics sets in.

Research to advance photoresponsive nanosystems

Besides other functionalities, architectures and units with promise for photoactive device elements are explored. Dr. Carlos-Andres Palma has, for example, developed refined concepts in the study of sunlight as a source of energy. If dye molecules, that is molecules that are able to absorb light of a particular wavelength, are brought with a complementary species to a monolayer sheet of graphene (a form of carbon organized in two-dimensional honeycomb structures), they will self-assemble into a network because of the large number of hydrogen bonds expressed. The dyes absorb light energy at a wavelength of 740 nanometers. As a result, electrons are displaced and induce a photocurrent, that can be detected with the help of a gallium counterelectrode. It is therefore possible to create a photoactive structure at the monolayer scale to convert sunlight into electricity. Dr. Joachim Reichert investigated how even individual large molecules can be used in practice for photovoltaic and photoelectrochemical purposes. The pertaining experiments show that it is possible to specifically control an individual molecular unit as a component of an optoelectronic nanoelement and use its natural functionality for photovoltaic applications. The researchers employed a special biomolecule called Photosystem I (PSI), which plays a key role in photosynthesis. Laser light is used to trigger a series of redox reactions, that is, chemical transformations in which one partner transfers electrons to the other. In the course of this sequence, one electron is transported along a transmission chain from one side of the protein to the other. The resulting photocurrent flow is surprisingly large – approximately 10 picoamperes or 10 trillionths of an ampere.

Heterogeneous catalysis and molecular nanowires

Exploring “true” chemical reactions on the nanoscale is the research focus of Dr. Klappenberger. In this work, the substrate surface, for instance a noble metal lattice, effectively replaces the test-tube. The reaction steps at the interface are vastly different to those that take place in solution environments. Here, the reactions go beyond the concept of self-assembly; proper electron pair bonds or atomic bonds between carbon atoms are formed. So how did the researchers approach the task? Everything revolves around organic molecules consisting mainly of a carbon skeleton with highly reactive carbon-containing end groups. Already at room temperature, bonds are formed between the molecules confined at a silver substrate. The metal surface becomes a catalyst that helps to lower the energy barrier for direct coupling between two terminal carbon atoms of neighboring molecules. What follows is an intricate reaction pathway culminating in atomic carbon-carbon bonds. This results in one- and two-dimensional nanostructures related to the hypothesized materials graphdiyne and graphyne, which are closely connected to the two-dimensional carbon lattice graphene. On account of some of its properties, graphene has limitations as an electronic component, whereas graphdiyne and graphyne are perfectly suitable for such applications. Physicists love to experiment, and in this case they had the idea of polishing the silver substrate surface to give it a step-like structure. Their thinking was that molecular chains would be able to form along the steps from the carbon-based molecules used. And that is exactly what happened. These chains could be described as wires, capable of acting as a medium to transport electricity for high-frequency components in the gigahertz or terahertz range. As for the two-dimensional graphdiyne structures and their nanopores, they could serve as a type of “prison” for guest molecules or as a hydrogen store in the batteries of the future.

The human factor

The basic research on new structures at the interface being undertaken in Barth’s Chair goes far beyond the projects described. The physicists are also exploring the know-how needed for application-oriented research. “High-level scientific output relies on innovative ideas and concepts. It can only be achieved by combining a dynamic work environment with excellent equipment mastered by promising doctoral candidates and postdocs,” comments Barth. They are encouraged with plenty of freedom to develop their own creativity and potential, but at the same time he is always available and ready to listen to any problems or questions. “His level of awareness is just amazing,” praises a young investigator from the research group.

Gerlinde Felix

Picture credit: Filser

> *“High-level scientific output relies on innovative ideas and concepts. It can only be achieved by combining a dynamic work environment with excellent equipment mastered by promising doctoral candidates and postdocs.”*
>
> *Johannes Barth*

Head of a scanning tunneling microscope which the group uses to manipulate and analyze the structures they created. The tip of the STM is pointing towards a copper surface mounted on the sample holder.