

# Calculating with Carbon

Monitors and smartphones that can be rolled and folded up, solar cells in clothing and cheap chips in packaging that store details about products – these are just some of the applications that could become possible in the future thanks to molecular electronics. At the **Max Planck Institute for Polymer Research** in Mainz, **Paul Blom** and **Dago de Leeuw** are optimizing the organic substances for this type of technology, paving the way for affordable, flexible and printable electronic components.

TEXT **PETER HERGERSBERG**

**S**erendipity has sparked many a scientific breakthrough, yet often enough, it also has a hand in helping a researcher find the field for which he or she was destined. In Paul Blom's case, this helping hand came in the form of an unusual workplace convention on the part of his first employer after he had graduated from college: the Dutch electronics manufacturer Philips stipulated that the company's researchers should work no more than six years in any given field. And so it happened that Blom one day found himself focusing on organic semiconductors, and no longer on inorganic materials, whose electronic properties he had been studying in the years prior to this switch.

"They wanted us to take on new fields of research with an open mind," says Blom, who has been serving as Director at the Max Planck Institute for Polymer Research in Mainz for almost a year now. "But I think it had to do

with the fact that scientists who are inexperienced in a particular field are easier to control," he laughs.

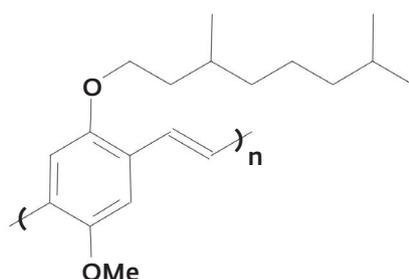
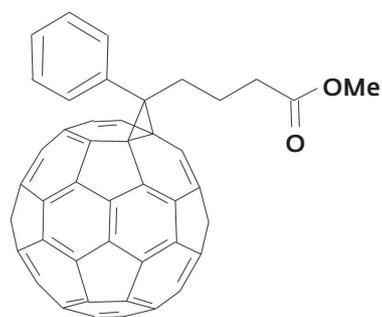
Philips has since abandoned this practice. However, it was precisely this convention that set Paul Blom on his path 18 years ago – a path that he embarked on rather unencumbered by prior knowledge, but is now pursuing with great success. The goal of his research is to develop a technology with which to manufacture lightweight, flexible microchips, light-emitting diodes (LEDs) and solar cells on all kinds of materials using a sort of inkjet printer. Both scientists and companies in the field of electronics hope to use such technology to exploit new applications (see also *MAXPLANCKRESEARCH* 3/2011, page 26): monitors and computers that can be rolled and folded up, solar cells on tents and backpacks, and clothing with integrated sensors that record medical data and alert the wearer of impending health risks. >



Photo: Thomas Hartmann



A stencil for solar cells: The researchers in Mainz are installing organic solar cells and LEDs on this substrate in order to metalize them as an electrode material. By using the respective template, they can identify the surfaces on which the metal has settled.



Light catchers: The polymer (right) derived from poly(p-phenylene vinylene) is composed of a long chain of the repeat unit pictured here. In solar cells, it absorbs light, which is used to excite electrons. The [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (left) – the characteristic building block of which is the buckminsterfullerene – takes up these excited electrons. This allows the latter to then travel to an electrode and flow as an electric current.

The realization of some of these ideas will be possible, or more easily possible, only because organo-electronic components can form using a principle that as yet can't be applied to the manufacture of chips, including those made of silicon: self-assembly. It is thanks to this principle that suitably designed organic molecules organize themselves to form the structures needed for electronic components.

Designing such components will be the focus of Paul Blom's work in Mainz, as will the charge transfer in molecules – a subject that runs through Blom's scientific career to date like a golden thread. He concentrated on charge transfer in gallium arsenide early on while writing his doctoral thesis, and later analyzed this same phenomenon in organic LEDs and solar cells while working at Philips.

Since charge carriers travel through organic molecules differently than they

do through silicon et al., this field that Paul Blom was about to explore was essentially uncharted territory – and not just for the physicist. “So far, the development of materials for organic electronics is based mostly on trial and error,” he says. For a long time, the only things that chemists had to go on in their search for organic semiconductors were fairly vague clues. They lacked the detailed understanding of the mechanisms of charge transfer in organic electronic components that they needed in order to design the molecules for specific applications.

### HOLES CAN TRAVEL FASTER THAN ELECTRONS

Paul Blom has already answered this question to a large extent with regard to organic LEDs and solar cells. “Some details remain unexplained, but we now have a very good understanding of how

charge transfer works in these components,” says the Max Planck researcher.

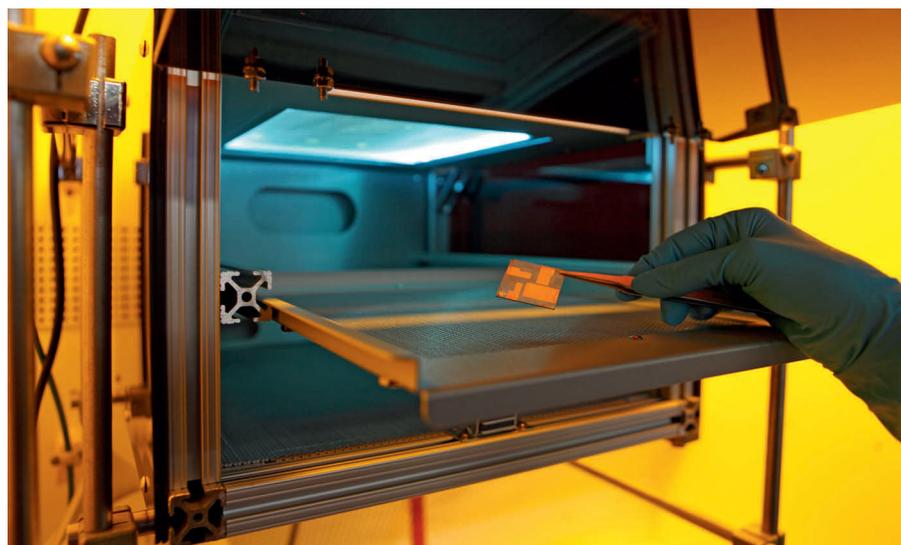
During his time working at the University of Groningen and the Holst Centre in Eindhoven, he systematically investigated the factors on which the mobility of the charge carriers in organic substances depend. Charge carriers are, on the one hand, the negatively charged electrons that flow through conductors or semiconductors, and on the other hand, the positively charged holes that mobile electrons leave behind on an atom or a molecule. After all, these holes can also travel through a material – sometimes even faster than the electrons, as Paul Blom discovered.

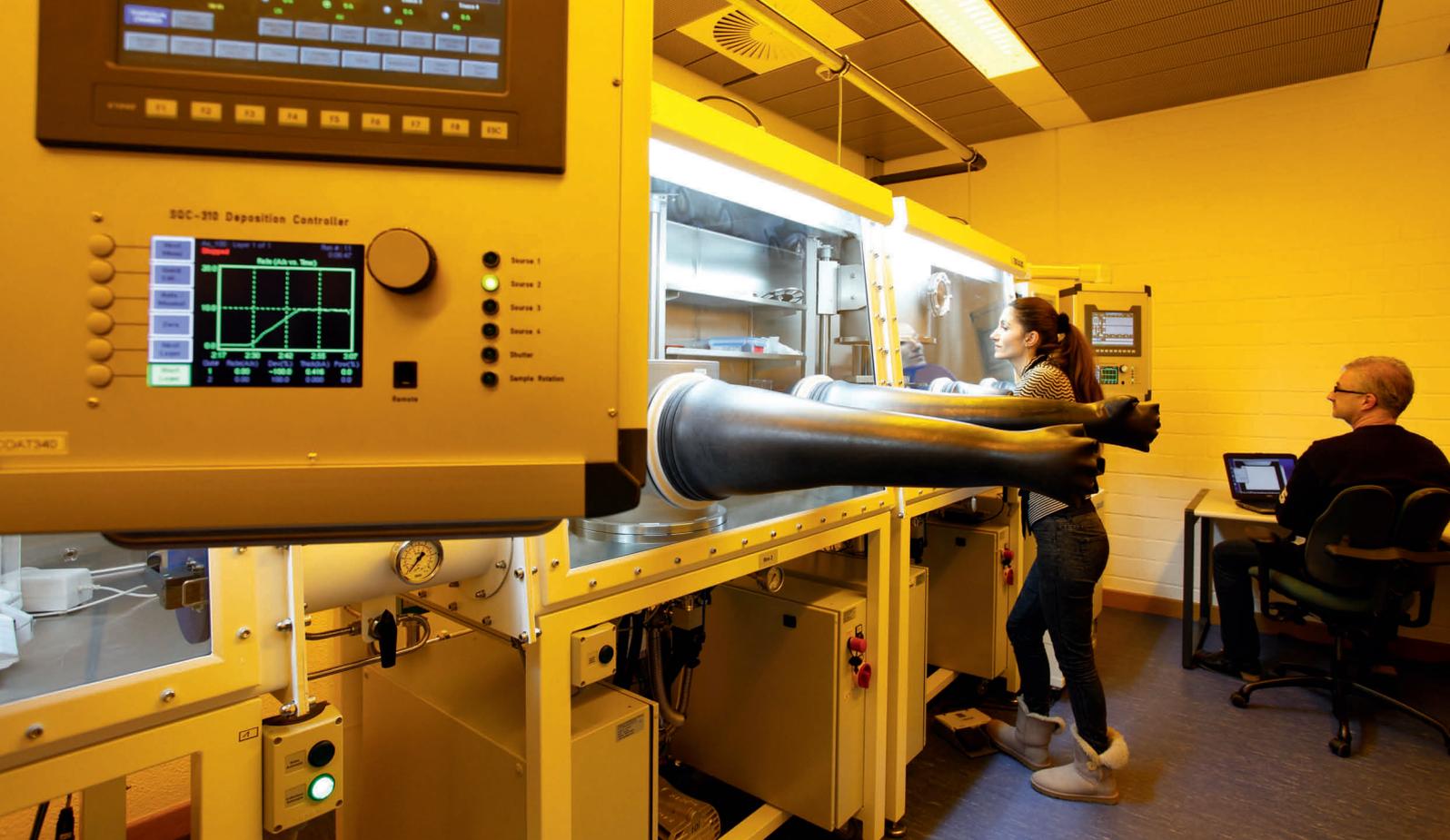
Moreover, in LEDs and solar cells, the mobile electrons and holes are the actual charge carriers: in the former they create light, and in the latter they discharge as an electric current. The prerequisite in both cases is that the electrons are excited to make them mobile, so that the holes – which are then also mobile – are left behind. That is why LEDs and solar cells are made from semiconductors that fulfill this condition. Molecular electronics requires organic semiconductors, and semiconducting polymers have proven to be the material of choice.

In an LED, an electric voltage yanks the electrons out of their original environment; in a solar cell, this task is performed by sunlight. Inside the LED, the electrons must then quickly find a suitable hole, and then fall into this hole, releasing their excess energy in the form of light. In the solar cell, that is precisely what must not happen. Instead, the charge carriers must travel into the power grid as quickly and – more importantly – as numerous as possible.

This means that, in both components, the crucial factor is the mobility of the charge carriers – that is, the strength of the current that flows

Light welds the polymer together: The Mainz-based researchers place wafers with the monomers of conductive chain molecules beneath a UV lamp in a chamber. The ultraviolet light causes the individual components to bond.





Conducting research in an inert atmosphere: In the glove boxes, connected to one another via airlocks, Irina Craciun can perform a series of steps to create electronic components and subsequently examine them. During the entire process, the material never comes into contact with air. In the background, Frank Keller reviews the operating parameters.

through the material (depending on an external voltage). In the semiconducting polymers, the holes are faster than the electrons, which is why they are responsible for most of the charge transfer. This is quite a heavy burden for them to bear: unlike the charges that zip through silicon, they virtually crawl through polymers, seeing as their mobility is one billion times lower. One thing that Paul Blom and his colleagues discovered is that, at least the higher the number of holes and electrons, the greater their mobility.

If the number of charge carriers is a decisive factor, then chemists must ensure that as many of them as possible can be created in a semiconducting polymer. Or that most of the current transporters present in a material don't disappear in the wrong locations. That is precisely what happens all too often in organic semiconductors, due to the fact that an irregularity in a polymer chain becomes a trap into which the electrons disappear – a bit like a jogger falling into a gaping pit that suddenly opens up in front of him.

Since the faults in polymers throttle the flow of the charge, Paul Blom then decided to concentrate on analyzing

these defects. “Our studies showed that the charge carriers in all conductive polymers get caught on the same type of defect,” the physicist says. “But we don't yet know exactly what that defect is.” Possible candidates include hydrogen or oxygen molecules adhering to the chain molecules.

### THE LOSS OF CHARGES CAN BE PREVENTED

Even though the exact location at which the charge carriers are lost still remains unknown, Paul Blom has some advice for chemists on how to prevent these disappearances. In order to understand how this trick works, it's helpful to examine why defects become traps for the charge carriers: in semiconductors, only electrons that have been charged with energy transport a current. However, since everything in nature strives to achieve the lowest possible state of energy, the particles want to shed the excess energy as quickly as they can. The defects allow them to do just that. This is because they still have free spaces in their electronic order, and the conducting electrons fall into them, releasing excess energy.

Paul Blom wants to take away the electrons' opportunity to rid themselves of excess energy, or rather, he wants to show others how this can be done: “With regard to organic LEDs, chemists must search for polymers in which the energy level of the conducting states is lower than that of the free states at the defects,” he says. The trap would then essentially hover above the electrons, and falling into such a trap is rather unlikely.

Preventing the charge carriers transporting the current from prematurely becoming lost at the defects is also imperative in the case of molecules for organic solar cells. After all, the aim is to harvest as many of them as possible in the form of an electric current using the photovoltaic elements. Therefore, the effectiveness of the elements, too, depends significantly on the type and distribution of the defects.

“If the movable charge carriers were created by light, they travel six nanometers on average before coming across a defect,” Blom explains. The charge carriers – the electrons and their corresponding holes – originate in long chain molecules when they are exposed to light with a sufficiently high

level of energy. The electrons can flow out of the solar cell only by jumping onto a second substance that is used in organic solar cells. Using the analogy of a popular German tradition, these molecules can be compared to the lanterns that children typically carry during St. Martin's Day processions: a buckyball hanging from the end of a rod-shaped molecule part. The structure of this buckyball composed of carbon pentagons and hexagons is reminiscent of the surface pattern of an old-style soccer ball.

### ELECTRONS DISAPPEAR AFTER SIX NANOMETERS

"The electrons are available for generating a current only if they manage to find a buckyball before coming across a defect," Paul Blom says. This means

that the molecules that create mobile charge carriers using light, as well as the molecules that transport the current away, must be mixed inside a solar cell in such a way that the electron needs to travel significantly less than six nanometers before being received by a buckyball – otherwise it will probably disappear at a defect.

Blom and his colleagues at the Max Planck Institute in Mainz have now set themselves the task of identifying the chemical defect that causes the disappearance of the charge carriers needed for LEDs and solar cells to work. The necessary substances for this undertaking are supplied by the chemists working in the department headed by Klaus Müllen. The theoretical studies that help explain their measurement results are provided by Kurt Kremer and his fellow scientists.

But first, the researchers in Blom's group will need specific types of laboratories in which to carry out their complex and meticulous studies. One such lab is a cleanroom in which they can produce the materials in a particulate-free environment to eliminate the risk of accidentally introducing additional defects into the components and then not knowing exactly what they are measuring. The cleanroom is being constructed in a part of the building that was previously used by Blom's predecessor and that has now been completely gutted. All that's left is the bare brickwork of a space about as tall as a gymnasium and roughly the size of a tennis court.

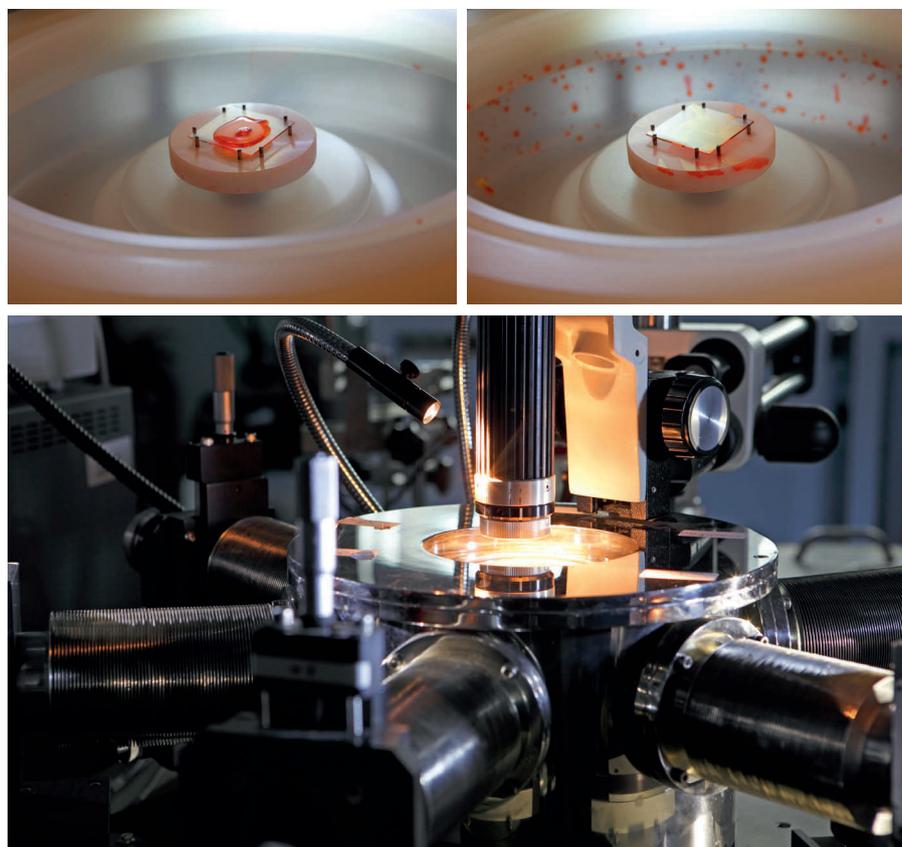
Paul Blom walks quickly through the labyrinth of institute corridors to another laboratory. This is where technicians are currently installing three glove boxes, each having the dimensions of a sizable aquarium and being connected via airlocks. The researchers can reach into the airtight chamber with the full-length rubber gloves mounted on the front glass panel. Upon completion, they will use one of these chambers with a noble gas or nitrogen atmosphere to construct electronic components out of air-sensitive substances, and the other two chambers to characterize the properties of said components.

The instruments of choice for producing solar cells, LEDs and chips made from organic semiconductors are metalizers and spin coaters. The former create the contacts needed to combine the organic materials with the metallic world of modern-day electrics and electronics for research purposes. The latter very evenly distribute the solutions of the organic substances onto a spinning disk.

The real work horse in Blom's group, however, is a voltmeter. The scientists use this instrument to characterize the physical properties of minute electric components and, in particular, to analyze the logistics of the electric charges within the structures. In a metal chamber roughly the size of a cake tin, the scientists bond their test components with needle-shaped electrodes attached to movable, jointed arms that are rather reminiscent of octopus tentacles. This allows them, for example, to measure the size of the electric current that

top: Turning (into) a thin film: In the spin coater, drops of a monomer solution are applied to a wafer and then rotated at high speed. The rotation causes the material to distribute across the substrate – as well as on the inside of the instrument itself.

bottom: Putting electronic components to the test: This chamber is used by the researchers in Paul Blom's team to analyze the electronic properties of solar cells, LEDs and data storage, and determine their respective current-voltage characteristics.



Photos: Thomas Hartmann (3)

the test materials allow to pass through (depending on the voltage applied).

Voltmeters, spin coaters and metalizers can also be found in the laboratories in which some of Paul Blom's colleagues have already begun working, because they don't require the strict conditions that exist in a cleanroom. Dago de Leeuw is one of them. He headed the first project to be completed in the new department: the development of a non-volatile memory composed of organic ferroelectric material.

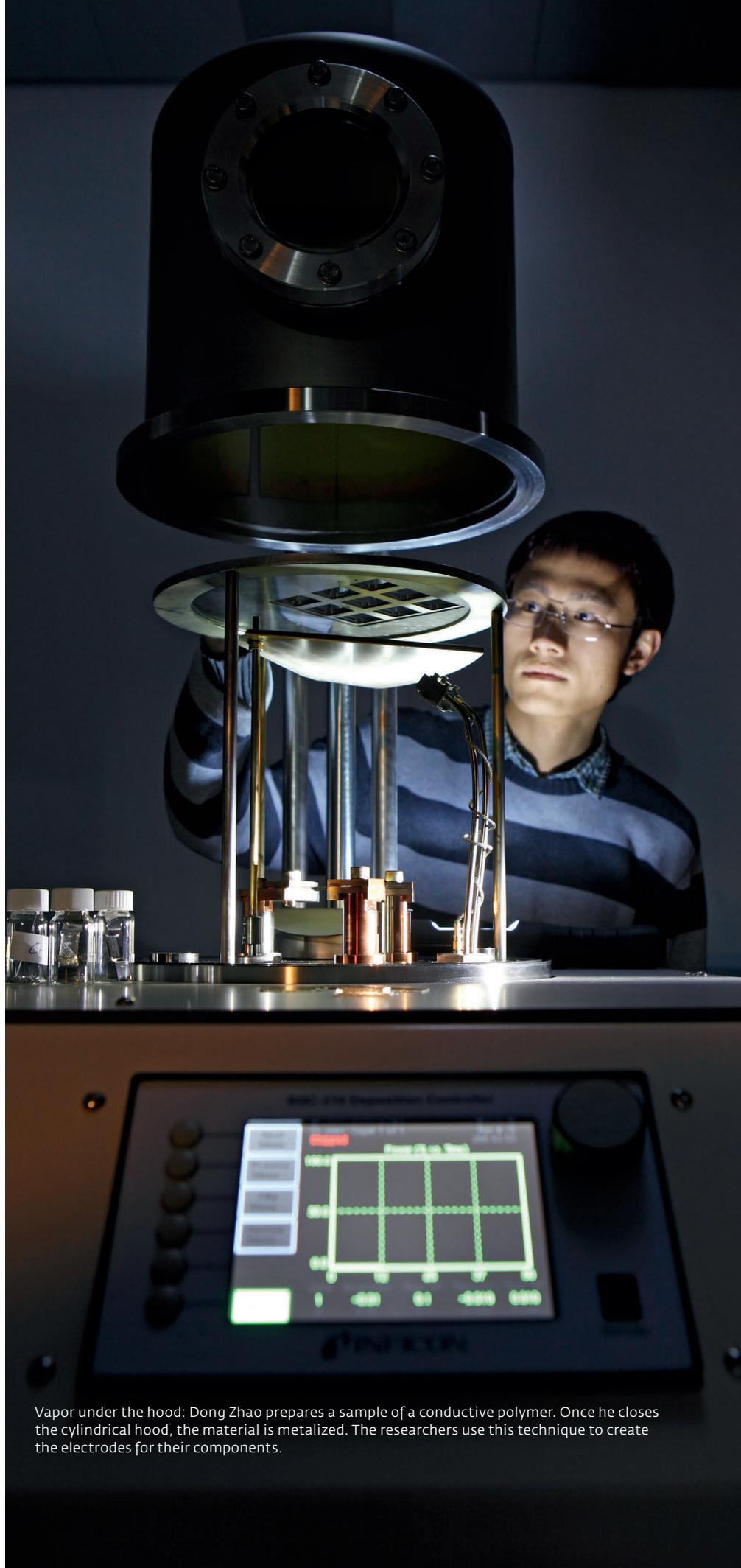
Non-volatile memories are the core components of every hard disk. They don't forget their stored content when the computer is shut down, but there is a limit to how densely they can be packed, and they can't be quickly re-programmed. Volatile random-access memories, on the other hand, can be very densely packed and grant quick access when computer programs need data fast. Yet they store information only when connected to electricity.

### A SOPHISTICATED DESIGN FOR ORGANIC MEMORIES

Ferroelectrics combine the best of both materials: they make data quickly accessible and can store information even without power. Just as the polarity of ferromagnets (to which modern non-volatile memories owe their good recollection) can be permanently reversed using a magnetic field, so ferroelectrics can also be switched back and forth between the zero and the one of a data bit using an electric field.

Materials scientists are currently studying numerous such materials (see *MAXPLANCKRESEARCH* 3/2011, page 34). Organic ferroelectrics stand out from this group because – just like organic semiconductors – their light weight and low cost makes them much more suitable for the production of versatile memories than is currently the case with inorganic materials. Silicon and the like can also be used to manufacture quick-access, non-volatile memories, but this still requires a complex procedure involving numerous individual steps.

In order to build non-volatile memories made from organic ferroelectric materials using a much simpler method, Dago de Leeuw and Paul Blom cre-



Vapor under the hood: Dong Zhao prepares a sample of a conductive polymer. Once he closes the cylindrical hood, the material is metalized. The researchers use this technique to create the electrodes for their components.

ated a sophisticated design for this type of memory. Just one of the many reasons why their concept could serve as a blueprint for memories with broad potential for technical application is that the researchers discovered a truly simple way to acquire such material. Other organic ferroelectric materials that the scientists first used to establish how non-volatile memories work are either expensive or explosive – not exactly desirable properties for a substance used in mass production.

“It has been known for some time now that the polymer PVDF, which is commonly used in membranes, can enter into a ferroelectric state,” explains Dago de Leeuw. “We found out that it can be put into this state using an electric field.” Furthermore, the team discovered a method with which the material – which forms rough sheets when conventional manufacturing techniques are applied – can be processed into thin, completely planar films.

Yet this synthetic material – also known by its full name of polyvinylidene fluoride – on its own isn’t sufficient for building practical, efficient memories, because while they are good at retaining information, they don’t divulge it freely. “That’s why we combined the material with the organic semiconductor P3HT,” says de Leeuw. Chemists also refer to P3HT as poly(3-hexylthiophene-2,5-diyl). The Mainz-based scientists embedded this material into a PVDF matrix in such a way that it fills the fine canals that traverse a thin layer of PVDF from top to bottom.

The researchers placed the ferroelectric material with the embedded semiconductor between two thin electrodes: silver at the bottom and a mixture of aluminum and lithium fluoride at the top. The underlying concept is clever: charge carriers can enter the semiconductor only from the silver, not from the combination of aluminum and lithium fluoride. But they can flow into the latter. The semiconductors therefore act as diodes: electric one-way streets.

### ELECTRIC ONE-WAY STREETS LEAD TO THE DESTINATION

How efficiently a current flows through the diodes depends on the polarity of the ferroelectric material coating the individual semiconductor canals. The ferroelectric material can be used to switch the resistance in the pores. And that’s precisely how the memory function works: a high resistance represents the one of a data bit, and a low resistance represents the zero, or vice versa. Since the polarity of the ferroelectric material is retained even in the absence of a current, the information isn’t lost, even when it isn’t constantly electrically refreshed. Moreover, a current that is too low to reverse the polarity of the ferroelectric material can easily be used to read the stored data.

But the only reason this concept works as well as it does is because Dago de Leeuw and Paul Blom devised the idea of the electric one-way street. “This arrangement prevents electric cross-talk – a problem prevalent in other memories

that work with an electric resistance,” says de Leeuw. Due to this electric cross-talk, the bits with a high electric resistance can’t be read reliably.

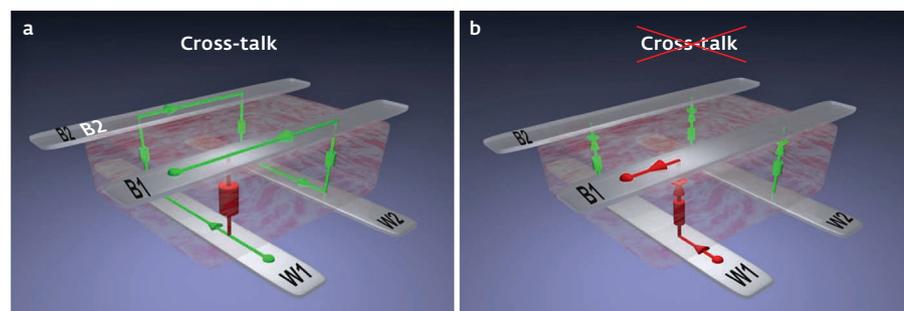
The reason this problem has arisen is that modern-day, and even more so, future electronics are advancing into such minute dimensions that the contacts between the memory and the outside world must be arranged in such a way as to take up the smallest possible amount of space. The data bits in the more or less efficiently conducting canals are therefore written and read via two lattices of parallel tracks, between which lies a layer of the actual storage material. The tracks of the lower and upper lattice run perpendicular to one another and always cross paths at one of the current-carrying canals. Each memory canal can thus theoretically be activated with a voltage that is in contact with one lower and one upper track.

In practice, however, the response of a canal with a high resistance isn’t easy to detect when the upper and the lower lattice are made from a material like silver, which allows an electric current to flow along the canals in both directions. In that case, the current that the voltage is supposed to make flow through a high-resistance canal simply looks for a new path via neighboring canals with a lower resistance. But the current can’t take this detour unless it is able to flow to the top and the bottom through the canals. This is precisely the type of behavior that is thwarted by the “electric one-way street” memory concept developed by the team of scientists in Mainz.

“We were thus able to design a memory that is non-volatile, easy to read, and can be very densely packed,” says Dago de Leeuw. The only factor limiting the data density is the width of the tracks and the minimum distance between them. One single storage point requires barely more than 20 nanometers of space.

Paul Blom and Dago de Leeuw have now set themselves the task of simplifying the production of the memory material, and they aim to do so by implementing one of the fundamental principles of nanotechnology: self-assembly. Today, the semiconductor industry carves out transistors, diodes or

Overcoming cross-talk in the memory: When the actual storage material channels a current up and down (a) between the tracks B<sub>1</sub>, B<sub>2</sub>, W<sub>1</sub> and W<sub>2</sub>, a data point with a high resistance (red cylinder) can’t be read reliably – the test current will simply look for a new route via neighboring low resistances (green cylinders). With silver electrodes at the bottom and contacts made from aluminum and lithium fluoride at the top (b), the storage material becomes a diode: an electric one-way street. This technique prevents cross-talk.





Fresh ideas for affordable and flexible electronics: Paul Blom (right) and Dago de Leeuw are contributing to the optimization of organic solar cells, LEDs and data chips by elucidating the underlying physical processes.

tracks from bulk material. This technique will grow increasingly difficult the smaller the structures become. The team of researchers in Mainz is therefore banking on the inherent tendency of many materials to adopt their own defined arrangement. The driving forces behind this phenomenon are the chemical and physical properties that cause the molecules to prefer certain configurations with respect to each other's position.

Paul Blom and Dago de Leeuw have already benefited from molecular self-assembly to gather and group organic substances into transistors and diodes. Next, they aim to apply this same principle to the more sophisticated structure of the non-volatile memories made from organic semiconductors coated in ferroelectric material. And they are planning further applications as well: "If, in the future, we can create complex structures by means of molecular self-assembly, we will be able to substantially simplify the production of electronic components," says Blom. Once this is achieved, if not sooner, organic electronics will be implemented on a large scale, facilitating applications that are currently uneconomical. ◀

### TO THE POINT

- **Molecular electronics** makes it possible to produce LEDs, solar cells and chips that are manufactured out of affordable, flexible materials and can be processed using a sort of inkjet printer.
- The mobility of electrons and the corresponding holes in organic semiconductors, and thus the efficiency of the resulting components, can be increased by using materials with an electronic structure that prevents the charge carriers from getting lost in defects.
- The thin layer of an organic ferroelectric material vertically traversed by semiconductor canals can be used to build non-volatile memories that can be densely packed and store data that can be written and read quickly and reliably.
- Electronic components just a few nanometers in size can be created from organic molecules using the principle of self-assembly, thanks to the molecules' chemical and physical properties, which cause them to form organized structures by themselves.

### GLOSSARY

**Ferroelectric material:** This term is based on an analogy with the ferromagnet. In a ferromagnet, magnetic moments can be aligned using a magnetic field, and they retain this polarity even outside of the magnetic field. In a ferroelectric material, an electric field shifts negative and positive charges against each other; they, too, retain their polarity even in the absence of the electric field.

**Charge carrier:** In metals and conductors in general, charge carriers are electrons that enable the transport of an electric current, for example. In metalloids, the electrons and holes are responsible for the current. Holes are created when electrons are excited, causing them to become mobile and then to begin to move. They leave behind a hole that can also move. When the electron falls back into a hole, energy is released in the form of electromagnetic radiation.

**Molecular electronics:** Made from organic materials, and therefore also known as organic electronics. Organic substances are composed of molecules that have carbon as their characteristic building block. These molecules can also occur as polymers, in which many structurally identical units combine to form chains or networks.