Aromatic **Chips**

Printable, flexible and low-cost – these are the properties that engineers hope to achieve with organic electronics. Researchers at the **Max Planck Institute for Solid State Research** and the **Max Planck Institute for Polymer Research** are investigating various materials that can be used to manufacture monitors that can be rolled up, or low-cost chips for mass-produced articles.

TEXT **TIM SCHRÖDER**

Banknote with chip: The transistors that the Stuttgart-based researchers manufacture from small organic molecules even operate reliably on a rough and crumpled banknote.

Photo: Axel Griesch

Perhaps Hagen Klauk should have been a physics teacher. In any case, he can explain things as well as they do. When he explains how electrons are transported through semiconductors, the process suddenly seems to be as clear and simple as a circuit with a battery and a light bulb. Klauk is standing in a dust-free cleanroom wearing a white, hooded overall. The ventilation hums quietly. “Of course, if the molecules in the semiconductor are too large or twisted, the electrons are obstructed and can’t really move forward,” he says, turning and bending and stretching his arms. Then he straightens up. “But if the molecules lie in a well-ordered arrangement and are very close to each other, the electrons can really whizz through the material.”

The question of how electrons can be speeded up has been occupying him for more than ten years. One might think there were more exciting things in life, but Klauk really gets going when he talks about his vision of a flat screen that can be rolled up, that is as thin as an overhead transparency and as colorful as a smartphone display. “A screen composed completely of flexible, elastic electronics that can be rolled up and put into your pocket – we are trying to do our part to make this a reality.”

LIGHT-EMITTING DIODES IN PERFECT ARRAY

Conventional displays consist of glass onto which a wafer-thin, disordered layer of silicon – the electronic material *par excellence* – is vapor-deposited. This type of display obviously can’t be folded. Not only because of the glass, but also because the silicon would flake off and crumble if it were rolled up or folded. This is why Hagen Klauk is interested in a class of materials that people didn’t really take seriously until the early 1990s: synthetic materials with electrical properties. These organic electronics consist mainly of carbon and hydrogen molecules – the most important constituents of plastics. But the flexible and robust electroplastic can’t yet compete with high-performance silicon because, among other things, the electrons don’t yet streak through the material fast enough.

Klauk and his colleagues specialize in transistors, which are key elements of all electronic components, and displays, as well. Transistors are a kind of valve for electric current. They regulate the flow of current in microprocessors and in the tiny light-emitting diodes of flat screens. Klauk takes a small magnifying glass from the desk. “Just take a look at the pixels on my smartphone with this.” Indeed, what can usually be seen as tiny, blurred dots on the screen enlarges to a perfectly ordered row of red, green and blue lines – very tiny, measuring just a few micrometers.

Every single one of them is a light-emitting diode, and each light-emitting diode is controlled by its own tiny transistor. When current flows, the diode lights up, brighter or darker depending on the current flow. A large screen uses millions of transistors, and to date, all of them, without exception, have consisted of vapor-deposited silicon.

Not so in Klauk’s cleanroom laboratory at the Max Planck Institute for Solid State Research in Stuttgart. He no longer uses silicon, but only transistors made of plastic – or to be more precise, of small, elongated hydrocarbon molecules whose electron distribution means they belong to the aromatic compounds. Light-emitting diodes from hydrocarbon molecules, the “organic light-

Photo: Axel Griesch

emitting diodes," or OLEDs for short, are already being produced on an industrial scale. Some electronics companies are using them in the first displays for smartphones and tablet PCs. But there are no similarly powerful organic transistors yet. These are precisely what Klauk wants to develop, because the flexible screen of the future needs both: flexible light-emitting diodes and flexible transistors.

Whether a transistor is made of silicon or hydrocarbons has, initially, no impact on its structure. First there is the substrate, the base material, onto which the layers of the transistor are deposited in a kind of sandwich. The substrate is usually glass. Klauk and his colleagues use wafer-thin film made of the plastic PEN, overhead transparency film. A thin layer of aluminum is vapor-deposited onto the substrate. This metal blob is called a gate electrode, which is used to control the current valve: it controls the flow of electrons through the semiconductor.

A thin insulating layer, the dielectric, comes next. This separates the gate electrode on the bottom from the semiconductor material on the top, which is subsequently deposited on the dielectric. Such a semiconductor can conduct electricity or act as an insulator, depending on its state. Its behavior is controlled via the voltage at the gate electrode. Of course, current flows through the semiconductor only when the material touches two electrical contacts between which the electrons can move. These contacts are called source and drain, and sit at the very top of the transistor.

Transistors with a silicon heart are established and mature. With the organic transistors – the organic field-effect transistors, or OFET – Klauk and his colleagues had to work on several issues at the same time. These included the migration speed of the electrons or, more precisely, their mobility in the semiconductor material. The faster they react, the faster the transistor can be switched. Light on, light off. Diode on, diode off. This must happen quickly in order for the image on the display to then appear with no flicker. The second point is the operating voltage. Some transistors require a voltage of between 50 and 100 volts for the current valve to open at all. This would be far too high for a display that could be rolled up and put into a briefcase. It should operate with three volts at most – the voltage of a conventional small battery.

LOW VOLTAGE FOR THE CURRENT VALVE

Some time ago, Klauk worked his way through a large number of publications by other scientists, searching for articles on the operating voltages of various organic transistors. The figures were enormous. Most of them were between 10 and 200 volts. A portable electro-gimmick would have been inconceivable. Some labs came close to the 5-volt mark, but none had gone below this. It is known that the voltage decreases especially when a thinner dielectric is used, but in a thin insulating layer, holes and defects are noticeable immediately. The performance of the transistor decreases considerably because the electron transport is obstructed. This marked the start of the search for a thin, yet non-leaky dielectric.

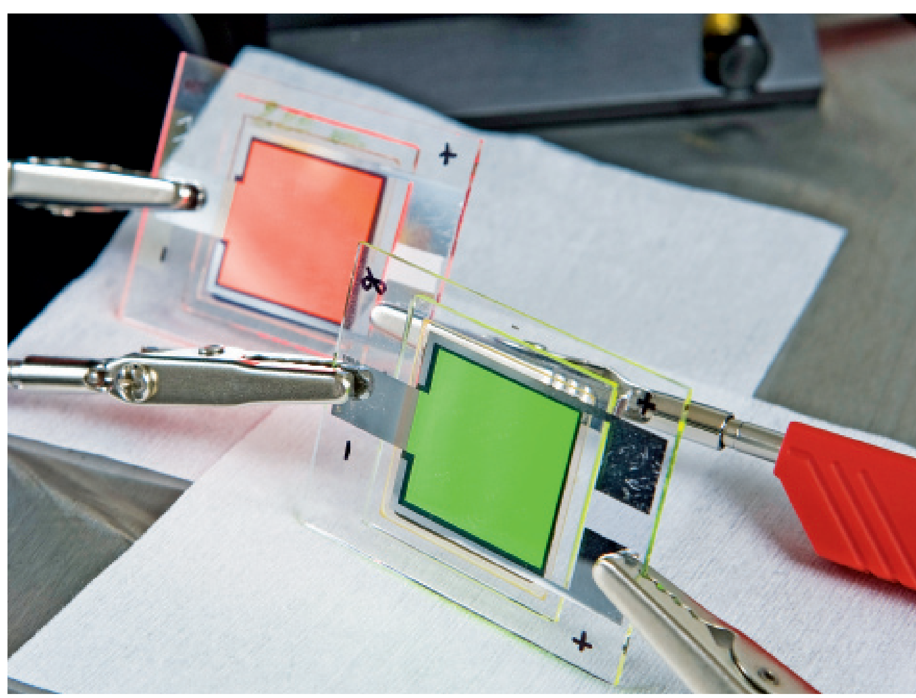
left | Hagen Klauk's team can conduct convincing experiments with organic semiconductors only in the dust-free atmosphere of a cleanroom. Ute Zschieschang (in the foreground) first carries out a visual check to determine whether the individual layers have properly deposited on a film.

below | Testing transistors: Hagen Klauk (top) works at the electrical testing station to electrically characterize an organic transistor. The substrate on which the researchers produced the transistors is the thin, circular polymer film at front left, on the sample table. The image below shows two organic light-emitting diodes (one red and one green) that can be electrically controlled with the aid of the transistor.

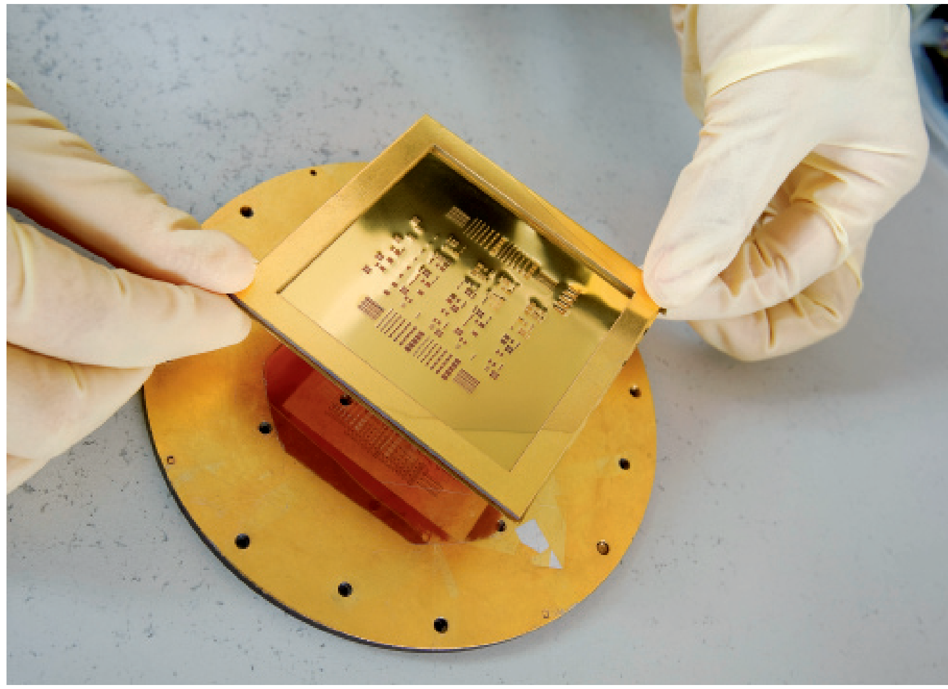
Klauk's colleague, Ute Zschieschang, came up with the groundbreaking idea. Earlier experiments with thin dielectrics composed of alkyl silanes, elongated molecules with a silane anchor group, had shown that silanes adhere well to silicon, but not to aluminum. Zschieschang leafed through scientific journals and learned that phosphonic acid anchor groups adhered significantly better to aluminum. Instead of the alkyl silane, Zschieschang now used alkyl phosphonic acid. This had the desired effect. These molecules lined up side by side on the gate electrode like the bristles of a brush, forming a wafer-thin, non-leaky dielectric only two nanometers thick. The operating voltage fell to below 2 volts!

But the transistors were still too slow, and their switching frequency too low. Although the human eye needs only 24 images per second in order for a film not to flicker and individual images to merge and form a stream of images, this would be nowhere near enough for a flat screen. Here, the image is compiled from top to bottom; the diodes are activated row by row. A large screen easily has more than a thousand lines that have to be switched on and off at breakneck speed. Ultimately, this is possible only when the transistor switches in the megahertz range, around one million times per second. But this was precisely what the organic transistors came nowhere near to achieving. A new semiconductor was needed.

For a long time, Klauk and his colleagues experimented with the standard semiconductor pentacene – an aromatic hydrocarbon. But pentacene is rapidly attacked by atmospheric oxygen. The semiconductor property is thus lost after just a few weeks. In 2007, Klauk happened to come across a pub-



Photos: Axel Griesch (2)



lication by researchers at the University of Hiroshima. They had synthesized a type of pentacene twin, which they implanted with two additional sulfur atoms: the semiconductor molecule dinaphtho-thieno-thiophene, or DNTT for short.

NEW SEMICONDUCTOR MAKES ELECTRONS MOBILE

The DNTT was extremely good at withstanding oxygen attacks. And Klauk discovered that this was by no means everything: the experiment showed that the electrons, the charge carriers, were much more mobile in this semiconductor – around three times as fast as before. The reason for this is primarily that the DNTT molecules arrange themselves in an orderly pattern. But it would still take a while before the birth of the megahertz transistor.

"The art is not only to choose the right materials, but also to design the whole manufacturing process," says Klauk. His cleanroom contains baking cabinets the size of a microwave oven, a variety of other over-sized equipment and a few microscopes. One of the most important tools is the vacuum unit – a black box with knobs and indicators. On the side hangs a sort of steel cheese dome. This is where the scientists coat the flexible plastic films with the organic transistors, layer by layer.

Basically, says Klauk, it's all quite simple. At the bottom of the vessel, the aluminum and the hydrocarbons are vaporized one after the other. The vapor wafts upward and condenses on the plastic film. A shadow mask with a very fine structure, a stencil, accurately controls where the substances are deposited. This is how the fine transistor sandwich structure grows, step by step. Only their years of experience enable the researchers to control the equipment in such a way that the substances are deposited in a perfect, unbroken and well-ordered manner one on top of the other on the plastic film. A layer of gold at the very top forms the source and drain contacts.

"I think we are probably one of the few cleanroom laboratories in Germany that can test organic semiconductor materials so quickly and thoroughly," says Klauk quite naturally and without a trace of vanity. Several industry companies and research laboratories regularly send him samples. "Who knows," says Klauk with a smile, "maybe we will be the ones who discover the perfect semiconductor for the flexible monitor of the future."

The Stuttgart-based researchers process their organic electronics at relatively moderate temperatures – less than 100 degrees Celsius, some substances even at room temperature. Silicon, in contrast, is processed at several hundred degrees Celsius. This is another reason why it is so difficult to unite silicon and flexible substrates. Plastic films do not survive the heat. Looking through one of the films that Klauk's team equipped with transistors and circuits, it's hard to believe that they really can conduct or control current. They are so thin, so insignificant and look like a normal printed overhead transparency.

But they are powerful. The research team in Stuttgart recently managed the transition to the megahertz rate – with the aid of a new shadow mask. During the coating process, Klauk previously covered the plastic substrate with a stencil that was likewise made of plastic. The fine transistor patterns are cut into this negative form with a computer-controlled laser. This is done by a specialist company. It is not possible to cut the shadow mask plastic arbitrarily fine, however, and for a long time, this limited the separation between the source and drain electrodes – it couldn't be made smaller than 10 micrometers. But the closer together the source and drain are, the faster the transistors switch.

It took Klauk a long time to figure out how to narrow the gap. Then, some time ago, he became acquainted with the microelectronics laboratory IMS Chips in Stuttgart, which uses a high-precision plasma process to etch pat-

Photos: Axel Griesch (2)

left: The researchers in Stuttgart use an evaporator to deposit organic semiconductors onto overhead transparency film, and also onto banknotes. They deposit the substances onto the substrate through a shadow mask in order to produce the structures of transistors.

terns into the membrane stencils with an accuracy of better than 1 micrometer. This brings the source and drain much closer together, and enabled Klauk and his colleagues to achieve the megahertz switching frequency for the first time last year.

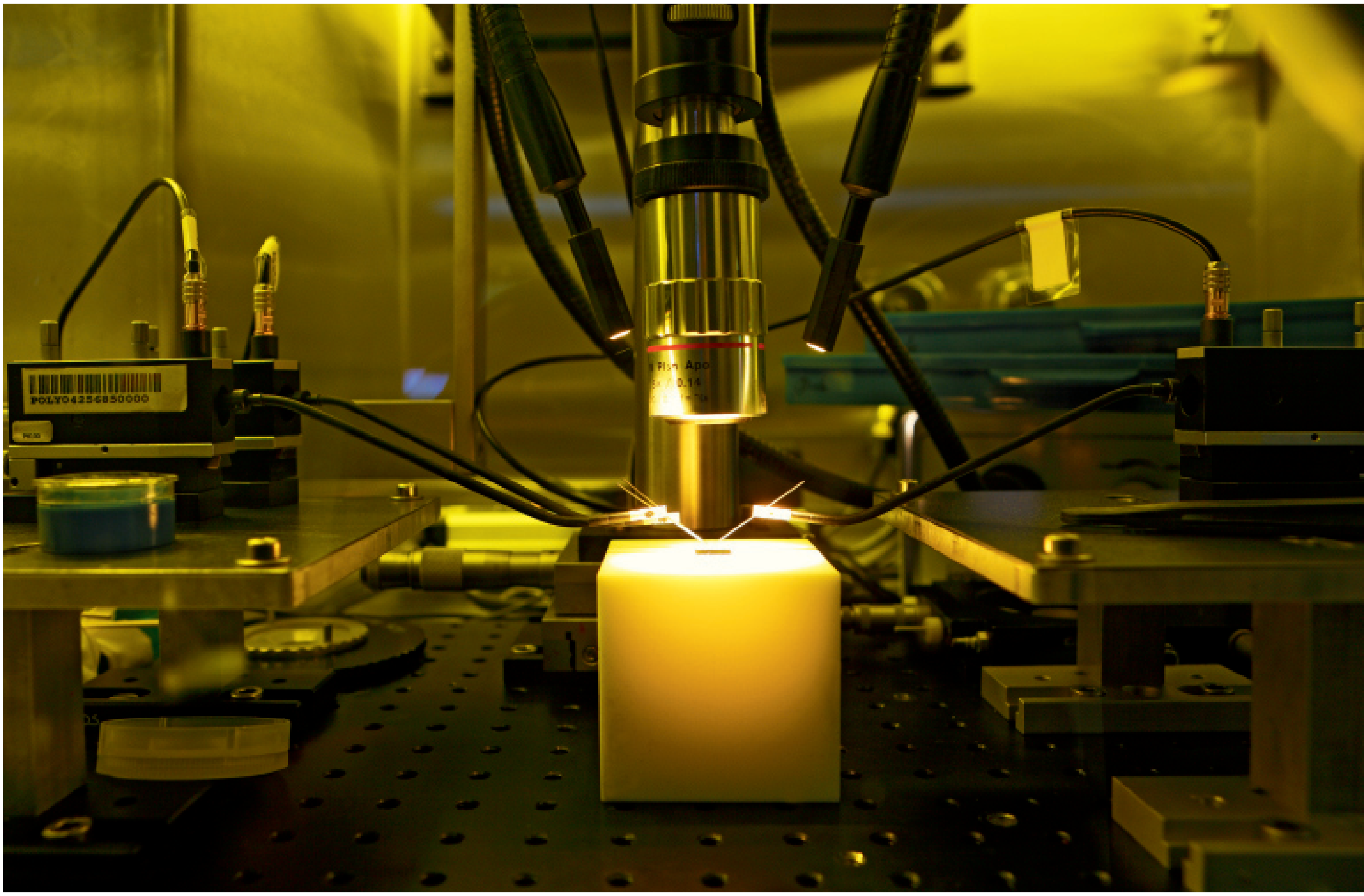
TRANSISTORS SURVIVE THE STRESS OF BENDING

The organic transistors from Klauk's cleanroom are now quite mature. They are robust and, above all, incredibly flexible. A year ago, his team caused a stir with transistors on a five-euro note. Plastic is smooth. Money is not. Although the structure of the cotton fibers in the banknote is rough, the transistors work surprisingly well. "We measured the small transistors individually – more than 90 percent were functional," says Klauk.

He then teamed up with Japanese researchers to go one step further. In an experiment, they bent the film at a sharp angle. "About a radius of one tenth of a millimeter," says Klauk. As if it were bent around the edge of a razor blade. The transistors survived this bending stress as well. The Japanese colleagues were already speculating about possible applications in the joint journal article. Such an electrical film, they said, could be rolled up to form a wafer-thin catheter to directly measure

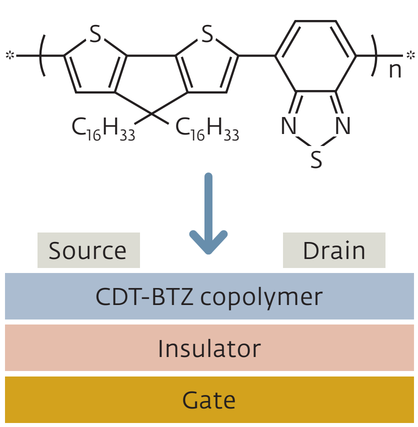
Ute Zschieschang and Hagen Klauk have made such progress with their organic semiconductors and their processing that they can now produce powerful electronic components on flexible and transparent materials.

Photo: Axel Griesch



top: At the Max Planck Institute for Chemistry in Mainz, researchers work with an apparatus that is similar to that of their colleagues in Stuttgart. However, they investigate long or branching polymer molecules as starting materials for low-cost electronic components.

bottom: An organic transistor operates according to the same principle as the established silicon transistors: The current flow between the source and drain electrodes is controlled via the gate electrode. The scientists in Mainz use the polymer CDT-BTZ, for example, as the semiconductor.



blood sugar in the veins or perhaps even to track down viruses.

Klaus Müllen, Director at the Max Planck Institute for Polymer Research in Mainz, has also been contemplating medical applications. Just like Klauk, Müllen is developing organic field-effect transistors, among other things. A synthetic chemist, he is primarily trying to create the perfect molecule for the organic semiconductor of the future. The strength of organic electronics, according to Müllen, is that they cost much less than silicon.

Instead of growing silicon structures in lengthy production processes, organic molecules can be produced essentially in a test tube. Some day it should be possible to print these substances onto plastic films, as with an ink jet printer – a process that would make this technology incomparably inexpensive. "I have this idea of small, low-cost transistors for RFID chips in radio tags, for Christmas cards that play music, or as cheap disposable sensors for medical tests," says Müllen. For quick blood sugar tests, for example. It would be conceivable that the glucose molecules deposit between the source and drain and disrupt the charge transport, thus providing an indication of the glucose concentration in the blood. "It will take a while for organic electronics to become established in the high-end segment, for screens, for example," believes Müllen.

WORLD RECORD IN THE MOLECULAR CHAIN

In the past, Müllen focused mainly on certain organic semiconductor molecules that were originally thought of as material for solar cells. Last year he established a world record here. Compared with Klauk's reasonably sized semiconductor substance DNTT, Müllen's molecules are true monsters, huge chains of molecules, so-called polymers, where the same molecular segments are repeated over and over again. A co-polymer bearing the difficult name cyclopentadithiophene benzothiadiazole, or CDT-BTZ for short, is particularly suitable for transistors.

These molecular chains combine two properties. They have segments

Photo: Thomas Hartmann Fotodesign

A pioneer of polymer electronics: Klaus Müllen and his colleagues use apparatuses like these to synthesize materials from which transistors, light-emitting diodes and solar cells could be produced in the future.

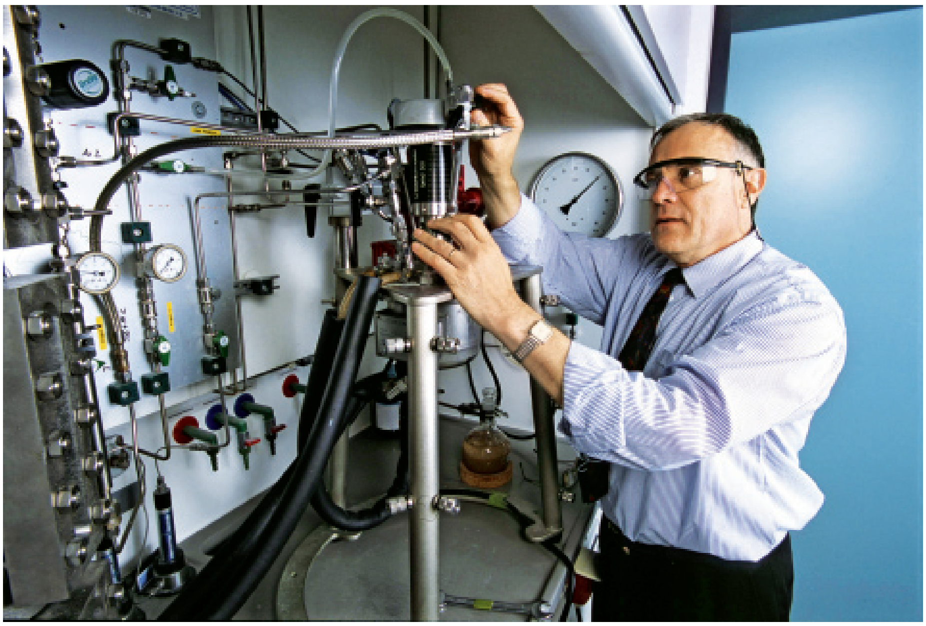


Photo: MPI for Polymer Research

that act as so-called donors, and segments with acceptor properties. Donors preferentially donate electrons, while acceptors tend to accept electrons. Both properties in the same molecule cause electrons to be passed on quickly, just like water buckets along a chain of firefighters.

Previously, it had been necessary to mix different substances with donor and acceptor properties in these types of semiconductors. CDT-BTZ provides this in a combo-pack. The result is impressive: The charge carriers migrate through the material around three times as fast as with today's best organic semiconductors and with Klauk's transistors. A world record. "However, it took a lot of experiments before we had completely redesigned the original CDT-BTZ molecule," says Müllen. He and his colleagues modified the branches, the ends of the molecule. "It's a mixture of experience and imagination that come together for such a development."

The charge transport also works so well because the long CDT-BTZ molecular chains huddle together like spaghetti in a packet of pasta, and thus form a type of racing track for the charge carriers. They only do this if they are manufactured correctly, however.

Unlike Klauk, Müllen does not deposit the substances in a vacuum. He wets the substrate with a polymer solution. As the solvent evaporates, the molecules arrange themselves to form the semiconductor layer. This also takes quite a lot of experience. The molecules must not clump together. They must converge to form an even layer. "The first one or two molecular layers are particularly important," says Müllen. "If their order is not perfect, a functional semiconductor layer cannot grow." Everything must be just right: the temperature, the speed with which the solvent evaporates. And the surface must be extremely clean.

With CDT-BTZ, Müllen has already synthesized an almost perfect molecule. And with his polymer solutions, he is already quite close to the printing process. Nevertheless, the hurdles are still high. The printable polymer semiconductor ink of the future must not run, not shrink and not crumble. It must adhere to the substrate perfectly and be flexible at the same time. No organic polymer electronics in the world provide this yet. Müllen and Klauk know that there is still quite a lot of work to do. Just how many years, neither of them knows. "I would, however, like to live to see the roll-up display made of organic diodes and transistors on the supermarket shelf," Klauk says, and laughs. ◂

GLOSSARY

Aromatic compounds
Chemical compounds such as benzene, for example. They usually have an almost planar carbon framework that contains at least one ring system with single and double bonds in an alternating arrangement. If the system has $4n+2$ double bonding electrons (n is an integer), they are delocalized to such an extent that single and double bonds can no longer be differentiated. This electronic structure favors the charge transport.

OLED
Organic light-emitting diode, which is constructed from semiconducting hydrocarbon molecules and used mainly in the manufacture of thin displays. It is less expensive than conventional (inorganic) light-emitting diodes, which consist of vapor-deposited silicon.

Field-effect transistors
Unipolar transistors in which only one type of charge is involved in the current transport, so, for example, only electrons flow from the source to the drain electrode. The current flow is controlled by the voltage applied to the gate electrode. Similar to a valve, this allows more or fewer electrons to migrate through the semiconductor. They are manufactured mainly from ultrapure semiconductor crystals.

OFETs
Organic field-effect transistors, whose semiconductor is constructed from organic materials. Although OFETs can be manufactured at a lower cost than conventional field-effect transistors, they are significantly more sensitive to external factors, greatly reducing their lifetime.

RFID
Radio frequency identification, which allows objects that are tagged with RFID chips as radio labels to be automatically identified and localized. This can greatly simplify data capture, for example from books in a library.