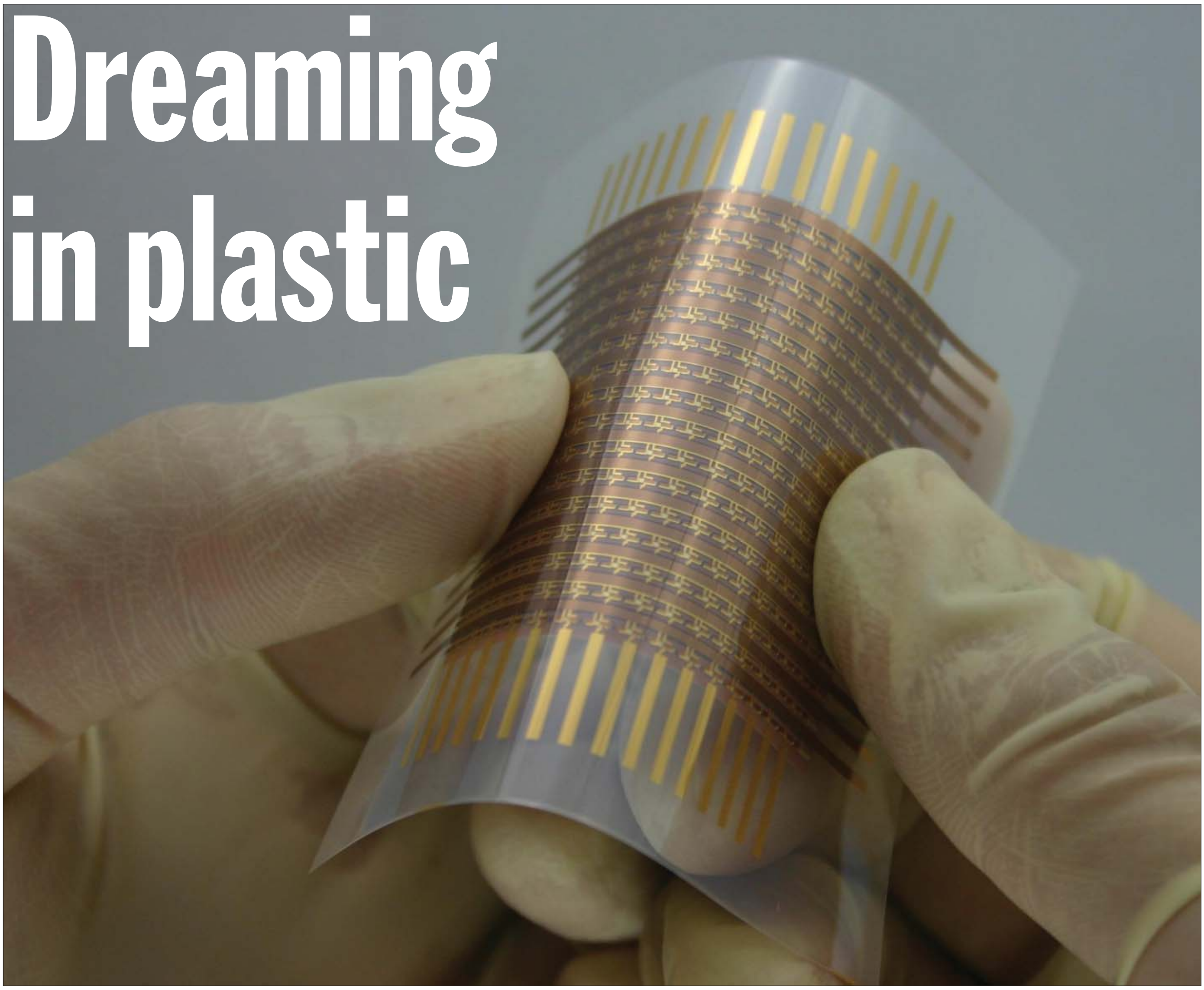
Dreaming in plastic



Takao Someya Group

Some 30 years on from the discovery of polymers that can conduct electricity, these fascinating materials are at last finding their way into our homes, as Marianna Korzhov, Rafi Shikler and David Andelman describe. Expect a whole host of innovative new applications to start appearing as plastic electronics comes of age

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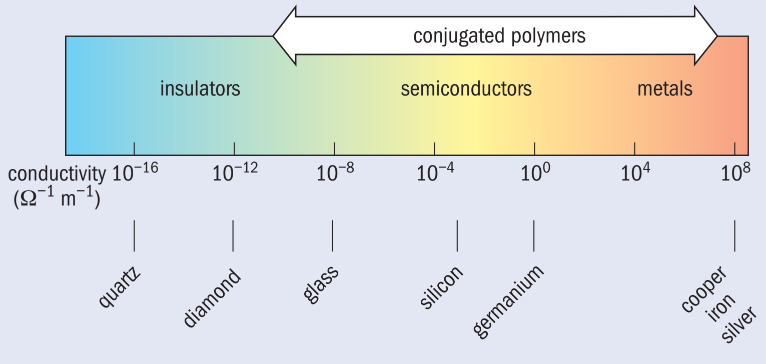
Plastic is one of the most versatile materials available. It is cheap, flexible and easy to process, and as a result it is all around us – from our computer keyboards to the soles of our shoes. One of its most common applications is as an insulating coating for electric wires; indeed, plastic is well known for its insulating characteristics. It came as something of a surprise, therefore, when in the late 1970s a new generation of plastics was discovered that displayed exactly the opposite behaviour – the ability to conduct electricity. In fact, plastics can be made with a whole range of conductivities – there are polymer materials that behave like semiconductors and there are those that can conduct as well as metals. This discovery sparked a revolution in the electronics community, and three decades of research effort is now yielding a range of stunning new applications for this ubiquitous material.

One of the most important properties of semiconducting plastics is that they can emit light in response to an applied voltage, which has led to the development of tiny, high-resolution colour displays for devices such as watches and mobile phones, and even a full-sized television less than 1 cm thick. Furthermore, displays based on plastic electronics are flexible, suggesting that, before long, they will be used to make electronic posters, billboards and even wallpaper. Eventually we might have plastic laptop computers that can be folded up, and some researchers are even trying to make plastic "skin" for robots that will give a sense of touch.

Electrons in motion

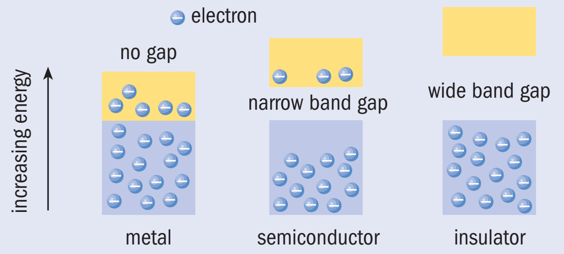
In order to conduct electricity a solid needs to contain electrons that are free to move around within it under the influence of an external electric field. The more of these "free" electrons a material has, the better it will conduct (see figure 1). Metals – the archetypal con-

1 A polymer for every occasion



The electrical conductivity of metals, semiconductors and insulators is distributed over a wide range of orders of magnitude, and conjugated polymers span the range from pure semiconductors to the most conductive metals.

2 The electronic band structure of solids



In solids, the electrons occupy energy levels called bands. In metals, the highest occupied band is only partially filled with electrons and the metal can conduct electricity. In insulators, the highest occupied band is filled with electrons and it is separated from the next empty band by an energy gap. If the energy gap between these two bands is small, then electrons can jump from the valence band to the conduction band at high enough temperatures, and the material is a semiconductor.

ductors – have lots of free electrons. In insulating materials, on the other hand, nearly all the electrons are tightly bound to atoms, so they cannot conduct. Semiconductors share the characteristics of both conductors and insulators – their conductivity can be controlled so that they can exhibit the behaviour of one or the other.

These behavioural differences are governed by the "electronic band structure" of the material in question (figure 2). According to quantum theory, electrons can only occupy specific energy levels, and in solids these energy levels form "bands", each of which can accommodate a specific maximum number of electrons. Electrons may not occupy the energy levels in between the bands, and the size of the energy gaps between the bands is determined by the material in question and its crystalline structure.

In metals the highest occupied band is only partially filled with electrons and is known as the conduction band. The electrons in it have space to move around and, under the influence of an electric field, they can continuously increase their energy by moving to higher available energy levels within the band. In insulators, however, the conduction band is empty and the highest occupied band is the valence band, which is completely full of electrons that cannot participate in electrical conduction.

Semiconductors also have an empty conduction band and a full valence band. Indeed, at low temperatures such materials do not conduct electricity at all. However, the energy gap in semiconductors is small enough that as the temperature rises, more and more electrons from the valence band can jump the gap into the conduction band. Once there, they can conduct. Even at room temperature, however, semiconductors never conduct as well as metals.

Semiconductors are widely used to build electronic components such as diodes and transistors, which regulate the direction and amplitude of electrical current. But to make practical devices, their electrical conductivity at room temperature must be increased by several orders of magnitude, which is achieved by adding small amounts of specific impurities to the material. These dopants either donate electrons to the conduction band or they trap some of the electrons from the nearly full valence band, thereby leaving behind "holes" that behave like positively charged particles and thus increasing the number of mobile charge carriers in the material.

Since the invention of the solid-state transistor in the late 1940s, doped semiconductors have been at the heart of the electronics industry, and semiconductor devices are continually getting smaller and more complex. Due to the way in which silicon chips are manufactured, however, there is a limit to how small they can be made and the size and mechanical properties of the devices is highly constrained. We cannot create large areas from silicon and, moreover, we cannot use this material to create bendable devices. The manufacturing processes are also expensive, requiring high temperatures and an extremely clean environment.

At a Glance: Polymer electronics

- Plastics are well known for their insulating properties, but in the 1970s researchers discovered a polymer that could conduct electricity
- This unusual behaviour arises thanks to the unique covalent-bond structure found in these materials, consisting of alternating double and single bonds
- Polymers with this structure – which is known as conjugation – have a range of conductivities and can replace metals and semiconductors in electronic circuits
- Electronic devices made from conducting plastics are cheap to manufacture and can be very light and flexible, opening up a host of new applications
- Polymer-based television screens are available to buy now, while in the future these materials will make possible things like thin, flexible laptops and even artificial skin for robots

Plastic fantastic

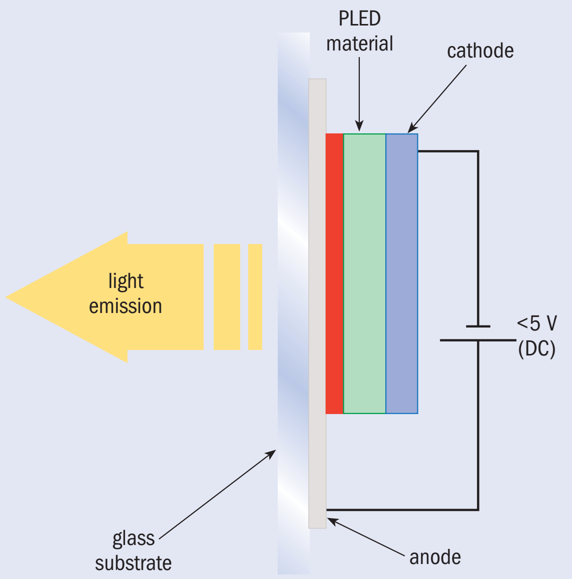
Plastics, on the other hand, are strong, light, flexible and easy to manufacture into any form required. A plastic that could conduct electricity, therefore, could revolutionize the electronics industry, making existing applications cheaper as well as opening the door to brand new ones, such as laptops that can be folded up. Despite the common dogma at the time that plastic materials were insulators, and therefore had qualitatively different electrical characteristics from metals, in the early 1970s Hideki Shirakawa at the University of Tsukuba in Japan serendipitously synthesized a polyacetylene film (made from chains of CH_2 groups) that exhibited several metallic properties.

Just a few years later, a collaboration involving Shirakawa and Alan Heeger (who is now at the University of California at Santa Barbara) and Alan MacDiarmid at the University of Pennsylvania, US, succeeded in manufacturing a plastic capable of conducting electric current. This breakthrough generated a huge amount of scientific activity, and led to the three researchers being awarded the 2000 Nobel Prize for Chemistry.

Plastics are artificial materials made of long molecules called polymers, which are chains of basic units linked together by covalent bonds, and the key to the trio's achievement was the application of a type of polymer architecture known as "conjugation" (see box below). In a conventional, insulating polymer the atoms forming the molecule are linked together with single covalent bonds, in which the electrons are tightly bound and cannot move around. Conjugated polymers such as polyacetylene, however, have alternating single and double bonds. The extra electrons from the double bonds are loosely bound and can move along the polymer chain and even hop between neighbouring chains. It is these "free" electrons that enable polyacetylene – and indeed all conjugated polymers – to conduct. With the help of appropriate dopants, conjugated polymers can be made to conduct as well as metals like silver and copper.

The hopping of electrons from one chain to another is a much slower process than the diffusion of electrons in a metal or semiconductor, so plastic-based electronics will never be able to equal silicon chips in terms of calculation speed and the capacity for miniaturization. But as it is cheap, flexible and simple to make and process, plastic can find its way to places that silicon will never reach. What is more, it can be designed to replicate the properties of both metals and semiconductors, meaning that in the future entire devices, from transistors to television screens, could be made cheaply from this versatile material.

3 All lit up



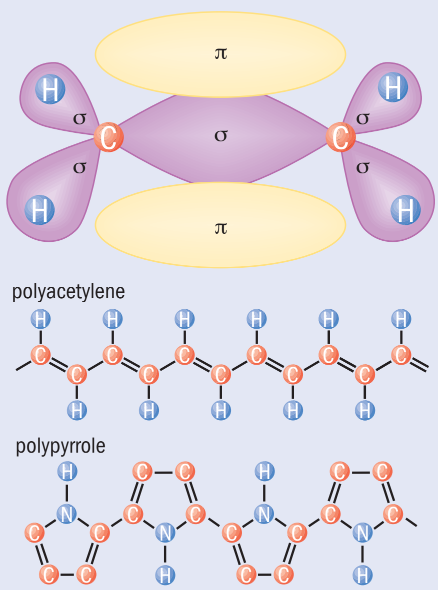
The polymer LED (PLED) has a simpler structure than a conventional LED, consisting of a thin layer of polymeric semiconducting material sandwiched between two metal electrodes. When a voltage is applied, the polymer glows and the light is emitted through the anode, which is transparent.

Let there be light

One of the most useful characteristics of semiconducting polymers is their ability to emit light when a voltage is applied. This property was first discovered in 1989 by Richard Friend and collaborators working at the Cavendish Laboratory at the University of Cambridge in the UK (*Physics World* June 1999 pp35–40), and since then a great deal of effort has been devoted to developing a new type of light-emitting diode (LED) made of polymeric material. In a polymer LED (PLED) a layer of polymeric material less than 100 nm thick is sandwiched between two metal electrodes. The

How to make a plastic behave like a metal

Polymers are long chains of basic units linked together by covalent bonds. These covalent bonds, which are created by pairs of electrons being shared between two neighbouring atoms, come in two types: sigma (σ) bonds are located in the plane between the neighbouring atoms; whereas pi (π) bonds are perpendicular to this plane (top). Usually a polymer will contain just single σ bonds, in which one pair of electrons is shared between two atoms. Conducting polymers, however, have alternating single and double bonds (in which two atoms share two pairs of electrons in one σ and one π bond), an architecture known as "conjugation". In the polyacetylene molecule (middle), for example, these conjugate bonds are between the carbon atoms that form the skeleton of the chain, while in other conducting polymers such as polypyrrole the conjugate bonds are within closed rings along the chain (bottom).



Regular polymers do not conduct because electrons participating in σ bonds are held very close (and are therefore tightly bound) to the carbon atoms and are not free to move around. In conjugated polymers, however, the electrons in the extra π bonds are loosely bound and can move both along the polymer chain and between neighbouring chains; it is these "free" electrons that enable conjugated polymers to conduct. Some conjugated polymers (such as polyaniline and polypyrrole) have a small amount of inherent conductivity at room temperature, but to achieve conductivity similar to that found in metals, conjugated polymers need to be doped. As with semiconductor doping, the insertion of the right kind of impurities can create positively charged holes in the valence band (or electrons in the conduction band), which then participate in electrical conduction.

4 Colour vision

Cambridge Display Technology

An example of coloured light emitted from specific polymers in response to being illuminated by white light, with no source of electricity (top). Each polymer has its own characteristic colour. A small television screen made of PLED mounted on a watch (bottom).

positively charged anode is a very thin layer of the transparent metal indium-tin-oxide and the negatively charged cathode is made of a regular metal. When a voltage is applied between the two electrodes, the PLED emits light through the anode (see figure 3).

A polymer LED works on the same principle as a conventional LED. The voltage that is applied between the two electrodes causes electric charges to be continuously "injected" into the PLED: electrons from the cathode and positively charged "holes" from the anode. These electrons and holes trap each other – in other words, the electron returns to the valence band from a higher energy level and fills up the hole. This recombination process releases energy in the form of a photon, the wavelength of which depends on the energy gap between the conduction and valence bands of the material in use (see figure 4).

Organic displays are ideal for use as television screens, and in small digital devices, traffic lights and illuminated signs that can bend around pillars

Polymeric LEDs, as well as other types of organic LEDs (OLEDs) that are based on small organic molecules, have several advantages over conventional LEDs. Firstly, their structure is very simple. Unlike inorganic semiconductor diodes, which require an interface (junction) between two materials with different dopants, the differently doped polymers in PLEDs can be mixed together in a solution and then spin-cast onto an electrode, meaning that they are inexpensive and easy to manufacture. They can also be made into thin, flexible layers that have large areas. Finally, their light emission is stronger than that of normal LEDs, and since the colour of the emitted light depends on the chemical structure, the molecules can be easily engineered to emit light in a variety of different colours.

These properties make OLEDs and, in particular, PLEDs an ideal basis for displays for all kinds of applications. Compared with other display technologies in use today, such as liquid-crystal displays (LCDs), organic displays can be made considerably thinner since they do not require background illumination – in fact, they can be less than 1 mm thick for some applications. They also turn on and off 100 times faster than conventional LCD displays, and they consume much less energy. A 27 inch OLED television, for example, consumes just 45 W. Also, in conventional LCD displays the light from separate sources needs to be sent through a coloured filter in order to obtain a pixel composed of the three primary colours, whereas polymer LEDs can emit monochromatic light on demand. This results in a brighter and clearer picture that can be seen from obtuse angles approaching 180°.

Organic displays are therefore ideal for use as television screens, and in small digital devices, traffic lights and illuminated signs that can bend around pillars. Today, PLED and OLED displays are being manufactured by companies such as Sony, Samsung, Kodak and Plastic Logic (which was spun-off from the Cavendish Laboratory) for applications including mobile-phone displays and even watch-sized television screens. Most current PLED displays have small screens, but larger PLED screens are beginning to come onto the market. Sony makes a 27 inch OLED television, for example, which can be bought for about $2500.

LEDs of all kinds are gradually replacing incandescent, fluorescent and halogen lamps, and it is generally believed that PLEDs and OLEDs will eventually take over a large fraction of this market. Currently worth about $1.5bn, the organic LED market is predicted to grow to $15.5bn by 2014, according to the technology analyst NanoMarkets. Indeed, in December last year Osram reported the development of a white OLED tile that can achieve an overall luminous efficacy of more than 20 lm per W at a brightness (luminance) of 1000 cd m^{-2}. (A typical 100 W incandescent light bulb can achieve about 15 lm per W.) Since it is easy to manufacture large, thin layers from plastic, we can even imagine one day having light-emitting wallpaper in our homes and other such spectacular applications.

Flexible friends

Brand new types of display may be the most visible consequence of polymer electronics, but perhaps the most significant step forward for the field was the development in the mid-1980s of an organic transistor. Transistors, which are the key component in the entire modern electronics industry, are usually made of silicon. But in recent years researchers have successfully manufactured polymeric devices made of plastic materials such as pentacene ($C_{22}H_{14}$).

The outstanding advantage of these organic transistors is that they are so easy to make. Building a sophisticated silicon chip involves complicated and expensive processes that must be carried out at high temperatures, under high-vacuum conditions and in rooms that are free of all pollutants. Organic transistors, in contrast, can be manufactured using quicker and cheaper processes that do not require such stringent conditions.

Using a device similar to a domestic inkjet printer, for example, it is possible to "print" polymer-based electric circuits within a few hours. In the summer of 2004 a group from Du Pont's research and development centre reported the first such printing on large surfaces (0.4 m^2) using a technique known as thermal printing. In this technology a laser beam produces a localized heat spot that binds the polymer onto the surface without damaging its chains. Such techniques, as well as inkjet and screen-printing methods, can be used to manufacture entire television screens, including all of the electronic circuits and pixels required.

Du Pont is not the only firm making organic transistors: Philips, Merck and Plastic Logic have also entered the market, incorporating the devices into flexible electronic components such as electronic paper (see figure 5). These devices still require a very thin metallic layer to form the contacts, but like any thin wire this is flexible and can be bent. In the future, polymer transistors could even make possible much more complicated electronic instruments, such as flexible laptops that can be folded up.

Even further in the future we could see the widespread use of robots with a sense of touch based on plastic electronics. In November 2003 Takao Someya and colleagues from Tokyo University announced that they had developed a flexible polymer sheet that was sensitive to pressure and could therefore mimic skin (*Proc. Natl Acad. Sci. USA* 2004 **10** 9966). The sheet was made from a compound of rubber and carbon, and incorporated organic transistors made of pentacene molecules. The electrical resistance of the rubber–carbon layer depends on how much it is compressed, since the conformation of a polymer chain (i.e. the way it is curled up) influences the mobility of its charges. In other words, the local resistance changes where the sheet is touched. This change in resistance operates an organic transistor at that location, which could be connected up to a robot's control system to enable it to "feel".

The team manufactured a system of 16 × 16 sensors (each of which was 3 mm^2 in size) containing transistors. This was made entirely from polymers and a layer of pentacene, except for gold electrodes and a copper coating attached to the rubber–carbon layer. The sheet could be rolled up to a diameter of 1 cm, thereby enabling the researchers to wrap it around the hand of a robot and sample the signals it received when local pressure was exerted (see figure 5). In principle this technology could be useful for any application that involves robots that need to touch or grasp an object. Imagine, for example, that you want a robot to hold a baby without harming it by gripping too tightly. Having pressure-sensitive skin would allow the robot to change the strength of its grip via a feedback loop linked to the pressure sensors.

Age of plastic

The robots most common today are unsophisticated devices that operate as lawnmowers and vacuum cleaners, or in industrial mass-production lines. But in the future, researchers expect robots and devices with artificial intelligence to be used for labour-intensive work like mining, traffic control, factory work and cleaning,

5 Bend me, shape me

Plastic Logic Inc.

Takao Someya Group

An electronic book made of organic transistors constructed from polymer thin-film transistors (top). A flexible sheet containing pentacene transistors, intended to create a layer of "skin" sensitive to pressure, is wrapped around a robot's hand to give it the ability to "feel" (bottom).

and these will undoubtedly include a score of displays and sensors made out of plastic electronics.

At the moment, however, the development of devices and instruments based on conducting plastic is still in its infancy. Researchers working in this area expect that, for many applications, these materials will gradually replace silicon and metals, and they may even make possible entirely new technologies, particularly in the field of bionics, which seeks to link up technology with biological systems. Conducting plastics bridge the gap between inorganic materials (metals and semiconductors) and organic materials (such as polymers and biological materials). They could offer a more efficient interface between living tissue and artificial replacements or enhancements, for example enabling researchers to build prosthetic limbs that can be linked directly to patients' muscles and nerves. Perhaps eventually such hybrid systems will be common place, connecting the living world, from the molecular level up to the level of an entire organism, with the world of technology. ■

More about: Polymer electronics

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R H Friend 2006 Polymers show they're metal *Nature* **441** 37

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