

Semiconducting polymers are moving out of the research lab and into the market-place as industry realizes the commercial potential of polymer-based LEDs, displays and photovoltaics

Polymer diodes

Richard Friend, Jeremy Burroughes and Tatsuya Shimoda

FROM CAR bumpers to bullet-proof vests – everyone is familiar with polymers as flexible yet mechanically strong materials. Less well known is the fact that some polymers can also conduct electricity and emit light. These semiconducting polymers, which have been intriguing researchers for the past 20 years, are now poised to enter the market-place. One of the most advanced applications lies in displays, where semiconducting polymers can be used as the active element in light-emitting diodes (LEDs). Philips, the Dutch electronics giant, has moved fastest to the market, and will commission a polymer-LED pilot production line at its factory in Heerlen in the Netherlands later this year. The firm will probably use the devices as back-lights for mobile phones and other portable electronic products. Another promising application of semiconducting polymers is in the field of photovoltaics, where they could be used as area detectors or solar cells.

The main reason for all this interest is that semiconducting polymers are easy to process. Semiconductor devices consist of a series of layers – electrodes, the active semiconductor material, insulators and so on – and it is attractive if they can be assembled, as polymers can, in solution.

Another advantage of polymer-based semiconducting devices is that it is easy to engineer the interfaces between the various layers to make working devices. In contrast, it is vital for the surfaces of inorganic semiconductors to be structurally regular at an atomic level. Any ruptured chemical bonds at the surface of these materials will have “non-bonding” orbitals that can stop the device from working. However, this problem does not occur in semiconducting polymers, which only have covalent bonds within each molecule. This is an important advantage, because it allows almost any combination of semiconducting-polymer materials to be used to build a device layer by layer. Semiconducting polymers are also interesting from a fundamental point of view because their electronic properties lie at the crossroads between traditional inorganic materials, such as silicon, and, for example, photoactive biomolecular materials.



Plastic fantastic – a polymer LED display in which the pixels have poly(phenylene vinylene) as the active element

Bonding basics

The common feature of all carbon-based molecular semiconductors is that they consist of alternate single and double carbon-carbon bonds. Such materials are said to be “conjugated” if it is possible to swap the positions of the single and double bonds and end up with a structure that still satisfies the chemical-bonding requirements for carbon. Carbon-carbon double bonds are formed when two of the three 2p orbitals on each carbon atom combine with the 2s orbital to form three sp^2 “hybrid” orbitals. These orbitals lie in a plane, directed at 120° to one another, and form three σ “molecular” orbitals with neighbouring atoms, including one with carbon. The third p orbital on the carbon atom, p_z , points perpendicular to the other hybrid orbitals. It overlaps with the p_z orbital on neighbouring carbon atoms to form a pair of so-called π molecular orbitals that are spread out or “delocalized” over the polymer chain. The lower-

energy π (or bonding) orbital is the valence band, while the higher-energy π^* (or antibonding) orbital forms the conduction band. This “band gap” gives the polymer its semiconducting behaviour.

But a polymer must also satisfy two other conditions for it to work as a semiconductor. One is that the σ bonds should be much stronger than the π bonds so that they can hold the molecule intact even when there are excited states – such as electrons and holes – in the π bonds. (These semiconductor excitations weaken the π bonds and the molecule would split apart were it not for the σ bonds.) The other requirement is that π orbitals on neighbouring polymer molecules should overlap with each other so that electrons and holes can move in three dimensions between molecules. Fortunately many polymers satisfy these three requirements.

Most conjugated polymers have semiconductor band gaps of 1.5–3 eV, which means that they are ideal for optoelectronic devices that emit visible light. They can also be chemically modified in a variety of ways, and a lot of effort has been put into finding materials that can be processed easily from solution – either as directly soluble polymers, or as “precursor”

polymers that are first processed in solution and then converted *in situ* to form the semiconducting structure.

The most widely used polymer is poly(phenylene vinylene) or “PPV”, which has a band gap of about 2.5 eV and emits yellow–green light. PPV is made up of benzene rings – the “phenylene” units – linked to one another via two carbons, which are each also bonded to a single hydrogen atom, or “vinylene” unit (figure 1). Researchers often modify PPV by attaching alkyl side-chains, such as $(\text{CH}_2)_n\text{CH}_3$, to the phenylene rings. This makes the polymer soluble in convenient solvents, such as xylene. It can then be easily processed directly from solution, using techniques such as spin-coating, whereby a drop of polymer solution is placed on a rapidly rotating substrate to form a thin, uniform film.

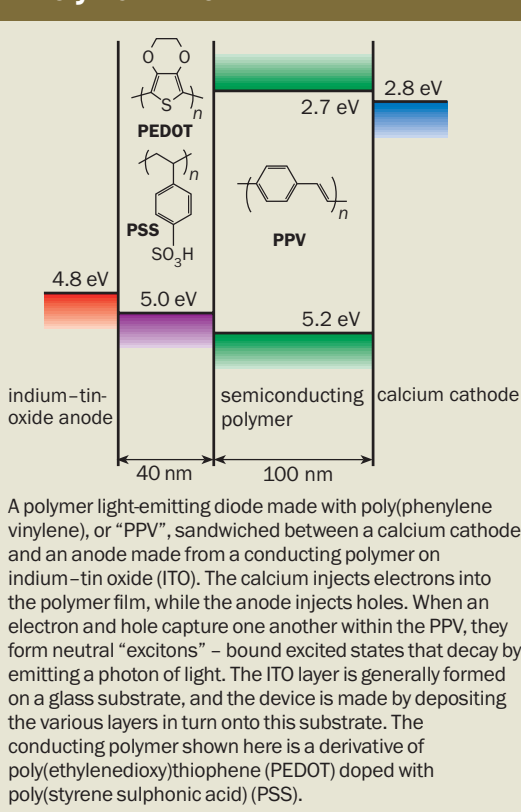
Polymer light-emitting diodes

Efficient polymer light-emitting diodes (LEDs) can be made from very simple structures. The first results, which two of the authors (RF and JB) reported in 1990, were made using a thin layer of polymer sandwiched between a pair of electrodes. The negative electrode injects electrons into the polymer film, while the positive electrode injects holes. When an electron and hole capture one another within the polymer, they form a neutral “exciton”, which is a bound excited state that can decay by emitting a photon. This process is known as “electroluminescence” since the emission of light is caused by the electric field between the electrodes. The negative electrode is chosen to have a low work function so that electrons can be easily injected, while the positive electrode has a high work function so that it can “suck in” electrons from the polymer. The hole-injecting electrode is usually made from indium–tin oxide, which is optically transparent and therefore allows the light to leave the device.

These early devices were not particularly good. They emitted very few photons relative to the number of charges injected, i.e. their “quantum efficiency” was low. However, seemingly similar structures have now been demonstrated with quantum efficiencies of up to 10% (figure 1). The improvements have been due to our better understanding of the chemistry of the electrode/polymer interfaces, which has allowed the newer devices to inject both electrons and holes easily into the semiconductor layer.

Indium–tin oxide would also seem to be the obvious choice as the positive, hole-injecting electrode because it is widely used in liquid-crystal displays and has a relatively high work function. However, indium–tin oxide is a notoriously variable material, with a work function that depends greatly on how the material was prepared. Although its work function can be as high as 4.8 eV, even this value is less than ideal since PPV has an ionization potential of about 5.2 eV. Holes from the indium–tin oxide layer would therefore have to overcome an

1 Polymer LEDs



energy barrier of 0.4 eV to enter the polymer layer.

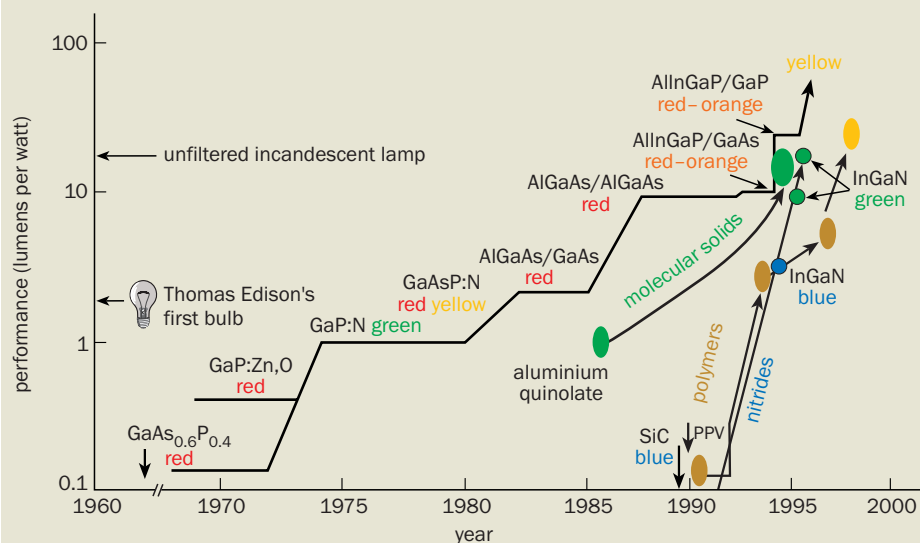
However, several groups have found that including a layer of conducting polymer between the indium–tin oxide and the light-emitting polymer helps to improve the injection of holes. (The extra layer is deliberately kept thin so that the device remains transparent.) One good example is poly(ethylenedioxy)thiophene, or “PEDOT”, a material that was developed by Bayer, the German chemical company. PEDOT can be mixed with poly(styrene sulphonic acid), or “PSS”, to form a stable and highly conducting charge-transfer complex, and this can be deposited from an aqueous solution to form a layer on the indium–tin oxide (figure 1). The PEDOT/PSS layer has a high work function (5.0 eV), which allows holes to be injected easily into the PPV since the barrier is now much smaller. Another advantage of the PEDOT/PSS layer is that it smoothes out the relatively rough surface of the indium–tin oxide,

thereby preventing any local short-circuiting that would otherwise cause the device to fail. An added bonus is that the surface of the PPV in contact with the PEDOT/PSS is lightly p-type doped by the PSS that builds up at the interface, which makes hole injection even easier.

What about the electron-injecting electrode? This should ideally be a metal with a low work function that matches the “electron affinity” – the difference in energy between the bottom of the conduction band and the vacuum level – of the PPV. Calcium has been widely used for this purpose. Its work function of 2.8 eV is close to the electron affinity of PPV (2.7 eV) and the barrier for electron injection is therefore small. As with the anode, the chemistry of the interface with the semiconducting-polymer layer is important. Calcium forms an ionic charge-transfer complex with the surface layers of the PPV, which n-dopes the polymer. Bill Salaneck and colleagues from Linköping University in Sweden have studied this behaviour with photoelectron spectroscopy, by depositing sub-monolayers of metal atoms *in situ* onto clean polymer surfaces in an ultrahigh vacuum. Other metals have also been used, including alloys of aluminium and lithium. The barrier for electron injection can be reduced still further by inserting a layer of alkali-metal fluoride, a few Angstroms thick, between the organic layer and the electrode.

As for the semiconducting polymer itself, it has several roles to play. It must allow electrons and holes to be transported. It has to allow electrons and holes to capture each other and form excitons. And it must also allow the excitons to emit photons. One important initiative in this field over the past few years has been the development of polymers that have high luminescence efficiencies. However, their discovery came as something of a surprise. Many conjugated molecules are highly luminescent when they are dilute – for example

2 LED efficiencies



The performance of inorganic and organic light-emitting diodes (LEDs), shown here in terms of the "luminous efficiency" in lumens per watt, has been improving steadily over the years. The semiconducting material in organic LEDs can either be a polymer or a sublimed film of small molecules, the latter having been developed by Kodak, Pioneer and other Japanese firms. The most advanced polymer LEDs now have efficiencies that rival those of traditional incandescent filament lamps, which are generally less than 20 lumens W^{-1} . Full-colour back-lit liquid-crystal graphic displays, in contrast, usually have efficiencies of no more than 2 lumens W^{-1} . (Figure updated from J R Sheats *et al.*)

light will be emitted from the triplet states. Since the triplets are at a much lower energy than the singlets, it is not even possible for an exciton to go from the triplet up to the single state and then emit a photon. (The triplets are at a much lower energy because the excitons in a polymer are localized to within than 10–15 monomers along a single chain.) Moreover, spin statistics mean that three times as many triplets as singlets are formed, so the quantum efficiency of a polymer LED cannot be more than 25%. This limit would be reached when every exciton in a singlet state emitted a photon, and when every pair of electrons and holes was captured perfectly. The highest efficiency so far obtained is 10%, which occurs when only half the singlets emit photons and not every electron captures a hole perfectly. This efficiency is already too high to be explained by a model that assumes that three triplets are formed for every singlet. It therefore seems likely that new models will be needed to explain

when they are in solution. (Indeed, the dyes used in dye-lasers, which are also conjugated molecules, have efficiencies of almost 100%.) However, most of these molecules are no longer luminescent in the solid state; solid-state laser dyes are dull, unpromising powders that give little hint of the vibrant fluorescence they show in solution.

This loss of luminescence is known as "solid-state quenching" and is caused by interactions between molecules in the solid that change the nature of the exciton. However, solid-state quenching is not a problem in many conjugated polymers, including PPV and its derivatives, which can have luminescent efficiencies of more than 50%. These improved efficiencies have allowed such polymers to be used as optical-gain materials in waveguide and laser-cavity structures. However, the results of these quenching studies were hotly disputed until very recently, and even now the explanations are probably not complete!

Brighter and better

Thanks to all of these efforts, the performance of polymer LEDs has advanced rapidly over the past two years (figure 2). Both organic and inorganic light-emitting diodes are now as efficient as a traditional tungsten light bulb, which, obviously, means that they could be used in lighting applications as well as displays. The working performance of a PPV diode is shown in figure 3.

So how much more improvement can we expect to see from these devices? The limit to the luminous efficiency in polymer LEDs is thought to be determined by the quantum mechanics of the excitons that are formed when the electrons and holes combine. However, this is the subject of intense debate right now. We know that when electrons and holes capture one another to form an exciton, the exciton can either be in a singlet or triplet spin-state. However, radiative transitions from the triplet state are forbidden, which means that no

how polymer LEDs operate, possibly involving spin-dependent electron-hole capture.

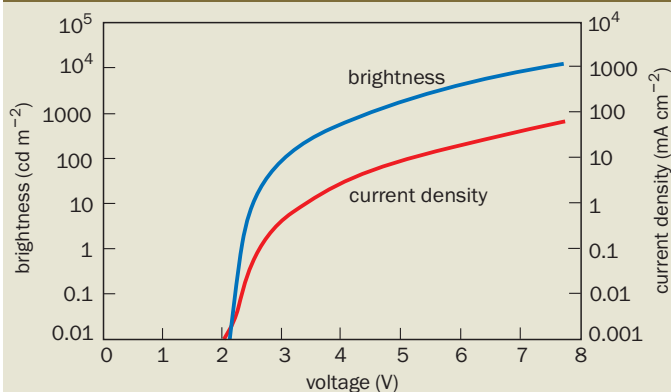
Polymer displays

Thanks to their high efficiencies, polymer LEDs are well suited for a wide range of applications, from simple back-lights to graphic displays. The first devices – such as those that Philips are developing – will be built on glass substrates and will be used for back-lights in portable electronic devices, such as mobile phones. However, the market will become much larger once these devices can be built on plastic substrates. At the moment it is impossible to use plastic substrates because barrier layers need to be inserted between the substrate and the device to prevent water and oxygen from entering, although researchers at DuPont in Delaware in the US are currently working on this problem.

Polymer LEDs will really take off if they can be used in full-colour displays, which have a market that is estimated to be worth as much as \$40bn a year. However, a lot of work is still needed to develop new polymers (or modified version of existing ones) that can emit red, green and blue light. One concern is that the emission spectra from polymers and other organic molecules are relatively broad, which may not allow absolutely pure colours to be obtained from polymer LEDs. Fortunately, however, the photoreceptors in the retinas of our eyes are also conjugated molecules, which means that they have a similarly broad absorption spectrum and the match between emission and absorption is satisfactory. We would not therefore notice that the colours are impure.

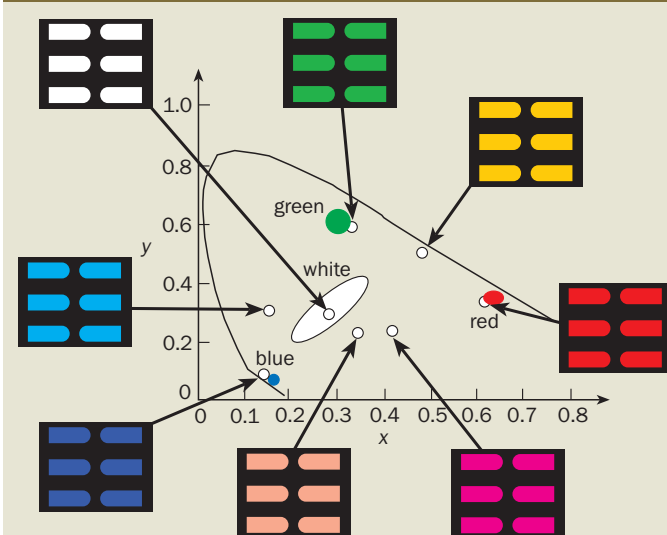
An important development in the synthesis of polymers has come from Ed Woo and colleagues at Dow Chemicals in the US, who have created a range of polymers based around the fluorene unit. Many other groups have also made progress, and at Cambridge Display Technology, the full range of red-, green- and blue-emitting polymers has now been obtained

3 Let there be light



Current and light output versus drive voltage for a green light-emitting polymer diode based on PPV with a structure similar to that shown in figure 1. The diode turns on when the voltage is 2 V and reaches a display-monitor level of brightness (100 cd m^{-2}) when the voltage is increased to 3 V. The power efficiency is then above 20 lumen W^{-1} . The broadly similar way in which the light and current density change with increasing voltage indicates that the diode has a constant quantum efficiency, near 20 cd A^{-1} , over the voltage range shown here. These devices could be used in everything from simple back-lights in portable electronic products to graphics displays. (Data courtesy of Heinrich Becker and colleagues at Aventis (formerly Hoechst) and Cambridge Display Technology.)

4 Colour on tap



Polymers based on poly(flourene) have been found to emit light over a range of colours. This "colour triangle" shows some of the colours obtained using different derivatives of the polymer. Pure red, green and blue light are at the apices of the triangle, with white near the centre. "Target" red-green-blue colours specified for the PAL colour co-ordinate system are also shown.

(figure 4). Each colour is obtained from a different variant of the polymer, with the band gap adjusted to provide the required colour. We find that if the device is built according to the design rules described above, the efficiency and the voltage needed to switch on the device is similar for each colour.

Graphic displays – such as television screens, computer monitors and palm-top devices – consist of several million pixels that need to be individually addressed. The "passive-matrix" scheme, in which the top and bottom electrodes are patterned to form rows and columns, is attractive because it is simple to make. Each pixel is addressed by applying a fixed voltage to each row in sequence, while a particular "data voltage" is applied to each column. The rectifying characteristics of these diodes removes cross-talk, and gives good performance for displays that need to show no more than "intermediate" information content, such as the screens in personal organizers. These devices typically have fewer than 100 000 pixels.

Beyond this, the need to drive each row for shorter times to higher peak currents becomes a limiting factor with passive-matrix displays, and there is now interest in using the "active-matrix" schemes that are found in high-quality liquid-crystal displays (LCDs). These displays use thin-film transistor circuits made from amorphous silicon to provide a "latch circuit" at each pixel, which maintains the correct potential at the liquid-crystal cell throughout the "refresh cycle" – the time between successive frames.

If we are to extend this approach to organic LEDs, the transistor circuit has to drive current through the LED. Unfortunately, this is not easy to do with amorphous silicon transistors because the electrons and holes move so slowly. However, amorphous silicon can be re-crystallized *in situ* to form polycrystalline silicon, which has much better mobilities; a device made from this material is therefore faster and can carry more current.

This type of device has already been developed for liquid-crystal displays, and the present authors – working with other

colleagues at the Seiko-Epson Base Technology Research Centre in Suwa, Japan – have shown that it can also be developed for polymer LEDs. Each pixel has two transistors – one provides the voltage latch as for the LCD screen and the other provides the current to drive the polymer LED. The polymer layers were formed by spin-coating to form a thin, uniform film. The display is monochrome, with the colour depending on the polymer used. Although the test circuit was, for convenience, a small structure just 2 inches in diagonal, it nevertheless had some 180 000 pixels, each of which could be individually addressed. The display even runs at high refresh rates (e.g. 85 Hz), since the polymer LED has a fast sub-microsecond response time.

The final step in developing a full-colour polymer-LED screen is to integrate the three primary colours together onto one screen. This requires the red, green and blue pixels to be "patterned", and although conventional lithographic techniques could be used, these are complex and expensive. We are therefore developing a new method, based on the ink-jet printing techniques of Seiko-Epson, in which the component layers for each LED colour – red, green and blue – are printed directly onto the substrate. The required resolution and uniformity is already available in current top-of-the-range ink-jet printers; the challenge now is to formulate semi-conducting-polymer solutions and to develop print heads that can produce these solutions.

Despite the rapid advances in polymer light-emitting diodes over the past two years, the rate at which the devices will be accepted by the market will depend both on performance and cost. Most of the requirements for a marketable device are already in place; Philips, for example, have shown that their LEDs will keep working for thousands of hours before they break down. But polymer LEDs must, above all, be cheap to make. This will be particularly important in advanced applications such as graphic displays, where the use of printing instead of lithography to make the devices will also be vital.

Photovoltaic diodes

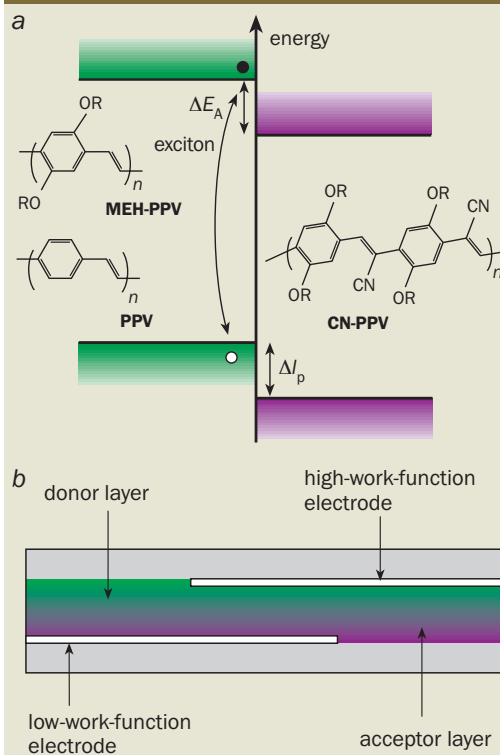
Another application of semiconducting polymers is as photovoltaic diodes. Photovoltaics are semiconducting materials that absorb light at energies above the band gap, leading to the separation of positive and negative charge carriers. These charges are collected at opposite electrodes, giving rise to an open-circuit voltage, or, with an external load, a photocurrent. At first sight, it does not seem that polymers would be suitable photovoltaics. As we have discussed, the excitons formed when an electron and hole capture one another – prompted either by absorbing a photon or by electrical excitation – are bound. So how can the exciton be encouraged to split? It turns out that by juxtaposing molecules that have different electron affinities, it becomes energetically favourable for an electron to transfer from one molecule to another. This process is called “photoexcited charge transfer” and causes the charges to separate. This donor–acceptor combination, in which one polymer donates an electron and the other absorbs it, can be viewed as a semiconductor heterojunction (figure 5a).

One polymer that has been used as an electron acceptor is cyano-PPV, or “CN-PPV”, which was developed by Steven Moratti and Andrew Holmes at Cambridge University. CN-PPV has electron-accepting cyano groups attached to the phenylene rings, which helps to lower the energy of both the valence and conduction bands. It therefore becomes energetically more favourable for the electron to transfer from the other polymer to the CN-PPV. Meanwhile, MEH-PPV has been used as an electron donor. This polymer is a derivative of PPV in which two of the hydrogen atoms on each phenylene ring are replaced by $\text{O}-\text{CH}_3$ and $\text{O}-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$. A heterojunction made from CN-PPV and MEH-PPV therefore causes excitons to split, with the holes moving into the MEH-PPV and the electrons moving into the CN-PPV. With appropriate collection of the charges, this system forms an efficient photodiode. Jean-Luc Brédas and colleagues at the University of Mon-Hainaut in Belgium are modelling the energetics of this type of heterojunctions.

However, this type of diode can only work if the difference in electron affinity between the two conduction bands is larger than the binding energy of the exciton when it is in one or the other polymer. This restriction rules out using pure PPV as the electron donor. Fortunately, this cloud has a silver lining; a heterojunction made from PPV and CN-PPV can be used to force efficient electron–hole capture at the heterojunction, to give very efficient LEDs.

This MEH-PPV/CN-PPV heterojunction provides a way of separating charge at a molecular level, and works very well for excitons that have been formed within reach of it. Unfortunately, excitons do not survive for long, and the characteristic distance over which they diffuse before they decay is much less than the thicknesses of polymer needed to absorb all the incident light. This greatly limits the efficiency of poly-

5 Polymers as photovoltaics



(a) Photovoltaic polymer diodes generate voltages by causing the excitons – electron–hole pairs formed after absorbing a photon – to split and redistribute their charge. But the excitons in polymers are bound, and will only split if there are two polymer molecules with different electron affinities near one another in a “heterojunction”. It then becomes energetically favourable for an electron to transfer from one type of polymer to the other. This diode has CN-PPV as the electron-accepting material and MEH-PPV as the electron-donating polymer. ΔE_A is the difference in electron affinity between the two materials’ conduction bands. ΔI_p is the difference in ionization potential of the two materials’ valence bands. An exciton will only split when ΔE_A is larger than the binding energy of the exciton. This condition is fulfilled for MEH-PPV but not for PPV itself. (b) The best photovoltaic polymer diodes have been obtained by fusing together the two polymer layers, which then form an interpenetrating network that helps the excitons to split. Excellent results have been obtained using a derivative of polythiophene, which absorbs light at 450–700 nm, and CN-PPV. Very high open-circuit voltages of more than 2 V can be obtained with a calcium cathode and a layer of PEDOT/PSS between the indium–tin-oxide anode and the CN-PPV.

mer photovoltaic diodes. For example, a diode made using indium–tin oxide as the electrode to MEH-PPV and aluminium as the electrode for CN-PPV, would only respond to photons absorbed within about 10 nm of the heterojunction. All the other photons would be wasted.

So is there a way of developing a more effective photovoltaic diode that does not just have the electron-accepting and the electron-donating layers back to back? It turns out that nature has developed very elaborate structures to achieve this, for example in the form of the “light-harvesting” antennae that bring excitons to the photosynthetic reaction centre in green plant matter. A much less sophisticated approach (and one that has taken rather less time to reach than nature’s efforts!) has been developed at Cambridge and also by Alan Heeger and colleagues at the University of California at Santa Barbara. The idea is to produce an interpenetrating network of an electron-accepting polymer and a hole-accepting polymer, so that the heterojunction is now distributed throughout the film thickness. This has been achieved by mixing the two polymers in a common solvent; when the solvent is removed, the polymers demix to form regions of one polymer and regions of the other. The best results have been obtained by laminating hole-accepting and electron-accepting polymers together (figure 5b). With a polythiophene derivative as hole-acceptor, this device absorbs sunlight relatively well, with a maximum quantum efficiency – charges collected per incident photon – of 28%. The maximum energy-conversion efficiency is 7% when the light shining on the diode is green, although this efficiency falls to 2% with sunlight.

Despite the progress to date, polymer photovoltaic cells are still very much at the research stage. Their performance will have to improve greatly before they can match inorganic photo cells. However, the results so far do reveal two very encouraging properties. First, the diode responds linearly

even when the intensity of the incident light reaches solar levels, which shows that the separation of electrons and holes is effective. Second, these polymer photovoltaic diodes produce very high open-circuit voltages. The maximum voltage is governed by the difference in work functions of the two electrodes, which can be more than 2 V with a calcium anode and an indium–tin oxide cathode coated with PEDOT/PSS. (Silicon cells, in contrast, have open-circuit voltages of less than 1 V.) This clearly shows that in spite of the crude processing methods, semiconducting polymers in these devices are remarkably free of defects that would have energies lying in the semiconductor gap. This is in marked contrast to the properties of comparably disordered inorganic semiconductors, where defects can limit the performance of the device.

Future prospects

Research into polymer diodes, which covers everything from chemistry to device physics, has made rapid progress over the past two years. The underlying science now shows more promise for future applications than previously suspected, and the effort put into making new materials has enabled devices with excellent characteristics to be built. The next few years could see this science base turn into large-scale technology – but getting there will require large investments in technology and marketing.

On the back of the prospect of new products, the efforts put into materials and device engineering is producing important dividends. In particular, the ability to process electronic materials in solution is opening up new paradigms for

manufacturing. We see “direct printing” (as a replacement for photolithography) as the new paradigm for polymer electronics. Indeed, ink-jet printing is just the start: developments in “soft lithography” will also make a huge impact. Allied with improved control of the “self-assembly” of ordered molecular or polymeric structures from solution, such as the bi-continuous network for solar cells, the potential for a radically different semiconductor technology in the future is great.

Further reading

- D de Leeuw 1999 Plastic electronics *Physics World* March pp31–34
R H Friend, D Bradley and A Holmes 1992 Polymer LEDs *Physics World* November pp42–46
R H Friend *et al.* 1999 Electroluminescence in conjugated polymers *Nature* **397** 121
M Granström *et al.* 1998 Laminated fabrication of polymeric photovoltaic diodes *Nature* **395** 257
J Kido 1999 Organic displays *Physics World* March pp27–30
J R Sheats *et al.* 1996 Organic electroluminescent devices *Science* **273** 884
H Spreitzer *et al.* 1998 Soluble phenyl-substituted PPVs – new materials for highly efficient polymer LEDs *Advanced Materials* **10** 1340
N Tessler, G J Denton and R H Friend 1996 Lasing from conjugated polymer microcavities *Nature* **382** 695

Richard Friend is at the Cavendish Laboratory, Madingley Road, Cambridge, CBE OHE, UK, and at Cambridge Display Technology, 181A Huntingdon Road, Cambridge CB3 0DJ, UK. **Jeremy Burroughes** is at Cambridge Display Technology. **Tatsuya Shimoda** is at the Seiko-Epson Corporation, Base Technology Research Centre, 3-5-3 Owa, Suwa-Shi, Nagano-Ken 392, Japan
