
Polymer electronics

I. D. W. Samuel

Phil. Trans. R. Soc. Lond. A 2000 **358**, 193-210

doi: 10.1098/rsta.2000.0527

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to:
<http://rsta.royalsocietypublishing.org/subscriptions>

Polymer electronics

BY I. D. W. SAMUEL

Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK

Polymers are well known as structural materials and electrical insulators. However, some remarkable polymers show conducting or semiconducting electrical properties, providing the basis for a new approach to electronics. The key advantages of polymers are that they are easy to shape and process, and that their properties can be tuned by modifying their structures or processing. When a voltage is applied to a semiconducting polymer it emits light, providing the basis of a new technology for flat-panel displays with excellent visibility. Initial applications could be for simple displays such as mobile phones, but very-large-area and even flexible displays are likely to follow. In addition to light-emitting diodes, polymer transistors and solar cells have been demonstrated together with conductors that can link these components. These elements provide the building blocks for electronics with unusual features such as the prospect of flexibility. Further advances can be expected from developing a deeper understanding of how the properties of these materials relate to their structure so that ultimately it should become possible to design materials with desired properties. The deposition of a range of polymer electronic devices by simple techniques such as printing is likely to extend the realm of electronics.

Keywords: optoelectronic; materials; polymer; semiconductor; light-emitting diodes; transistors

1. Introduction

Polymers, or plastics, are familiar materials found throughout everyday life. Polymer molecules consist of many repeat units, and the enormous range of possible repeat units gives an almost unlimited variety of polymeric materials. This gives great diversity, and applications of polymers range from compact discs to bullet-proof vests and from cling film to car tyres. Biological polymers such as DNA, proteins and cellulose form the basis of life itself. One of the key reasons for the widespread use of man-made polymers is the ease with which they can be processed into almost any desired shape or form. They can be moulded into a particular shape, extruded to make tubes or films, or spun to make fibres. A further advantage of polymers is that their properties can be controlled by modifying their chemical structure. To date, polymers have been widely used as structural materials (e.g. for furniture, computer housings, etc.), for packaging and as fabrics and films.

There are some remarkable polymers that can conduct electricity, opening new directions in electronics and polymer science. They offer the prospect of materials that combine novel electronic properties with the ease of processing of polymers, and whose properties can be tuned by chemical modification to give desired features. This new class of electronic materials means that we can now dream of giant flexible

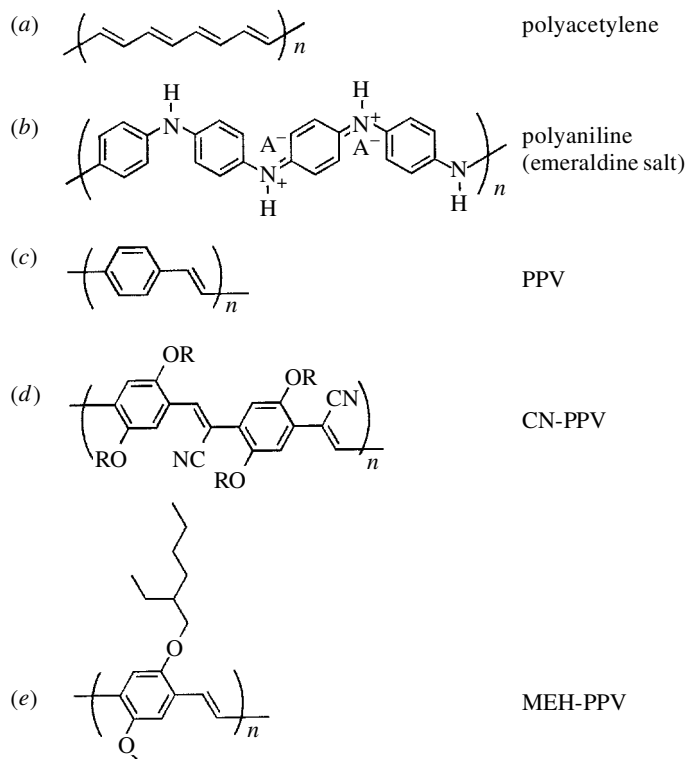


Figure 1. Chemical structures of a selection of conjugated polymers.

displays and electronic circuits made by printing. In this article, we shall look at the remarkable developments that have taken place in this field, giving plastic transistors and light-emitting diodes (LEDs), and then consider the ingredients that will fuse to give future innovations.

The vast majority of polymers are electrical insulators. However, a special class of polymers, known as conjugated polymers, exhibits semiconducting properties. ‘Conjugated’ means that the molecules have a backbone containing alternating double and single bonds. The simplest example is polyacetylene, which is shown in figure 1*a*. Electrons in the double bonds are in π -orbitals, which overlap along the polymer chain. These electrons are mobile and therefore provide a way of carrying current. There are two electrons in π -orbitals per repeat unit of the polymer chain, and because of the Pauli exclusion principle, this leads to a filled band, and semiconducting electronic properties. The electrons can move easily along a polymer chain, but with difficulty between neighbouring polymer chains, so that these systems have one-dimensional character. An enormous range of conjugated polymers has been synthesized and some examples are shown in figure 1.

(a) *Conducting polymers*

The initial interest in conjugated polymers in the 1970s was in their potential use as conducting materials. Conjugated polymers can be doped, in analogy to inorganic

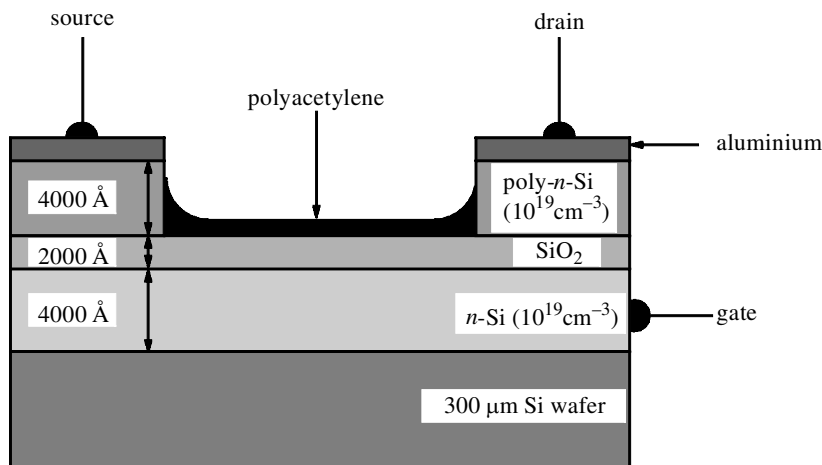


Figure 2. Cross-section of an FET using the conjugated polymer polyacetylene as the semiconductor (Burroughes *et al.* 1988).

semiconductors, and very high levels of doping lead to many free charge carriers and, hence, high conductivity (Chiang *et al.* 1977). It was suggested that it might be possible to make polymers with the conductivity of copper and the strength of steel. High conductivities were achieved in polyacetylene, but have not been exploited as the material is very sensitive to exposure to air.

A promising alternative is polyaniline (figure 1*b*), which can be doped to give a conducting polymer. By choosing an appropriate dopant, polyaniline can be rendered both soluble and conducting (Cao *et al.* 1992), but with the important advantage of much-improved stability in air. The conductivities are not high enough to replace metals, but they do open up a range of applications where only modest conductivities are required. Examples include capacitor electrolytes, conductive coatings for electrostatic speakers, antistatic packaging, electromagnetic screening, and stealth technology. In addition, conducting polymers can be used to make transparent conductive coatings for display applications.

(*b*) Semiconducting polymers

During the 1980s, interest in the semiconducting properties of conjugated polymers developed. The way in which the polymers respond to light and the addition of charge was studied, and the results were related to the one-dimensional character of the materials. As conjugated polymers are semiconductors, they can be used to make semiconducting electronic devices, such as field-effect transistors (FETs), LEDs, photodiodes and solar cells.

(*c*) Field-effect transistor

One of the first polymer devices was an FET (Burroughes *et al.* 1988). The structure of this device is shown in figure 2. It consists of a heavily doped silicon substrate, with an oxide insulating layer onto which a film of polyacetylene is deposited and contacts evaporated. The highly doped silicon acts as a metallic contact. In a transistor, the current flowing between two contacts (the source and the drain) is controlled

by the voltage applied to a third contact (the gate). In the polymer FET, the gate voltage is applied to the doped silicon. The resulting electric field changes the charge carrier density in the polyacetylene layer, thereby controlling the current flowing through it from the source to the drain.

An attractive feature of this type of device is its relatively simple fabrication. All-organic transistors have also been made (i.e. without a silicon substrate), giving even simpler fabrication (Garnier *et al.* 1994). In addition to ease of fabrication, polymer electronic devices often have additional features not present in their inorganic counterparts. In the case of the polymer transistor, injected charge forms states in the band gap that can absorb light, so that modulation of the gate voltage could be used to modulate the transmission of light through the device. Modulation of light is needed for encoding signals in optical telecommunications, although in the case of a polymer transistor the process is not fast enough to be useful. An alternative transistor involves using an organic material as the gate of the transistor. The organic layer can be doped by gases in the atmosphere, causing a large change in the current through the device when it is exposed to certain gases (Barker *et al.* 1996). This device can be used as a gas sensor, and by using a few such devices with different sensing layers connected to a neural network, it has been possible to make an 'electronic nose', i.e. an electronic device capable of distinguishing between different smells.

(d) *Light-emitting diodes*

In spite of the interesting developments outlined above, a decade ago, only a tiny fraction of the scientific community was aware of the possibility of polymers having semiconducting electronic properties. The situation has been transformed by the serendipitous discovery in Cambridge that polymers could be used to make LEDs (Burroughes *et al.* 1990). The Cambridge group found that when a voltage was applied to a conjugated polymer film in between two suitable contacts, the polymer emitted light. The polymer used was poly(*p*-phenylene vinylene) (PPV) (see figure 1c) and it gave a yellow-green glow. Although the efficiency of light emission was very low, its enormous potential was quickly recognized, and led to an explosion of interest in the field.

A simple polymer LED is shown in figure 3. It consists of a conjugated polymer film in between two electrodes. When a (DC) voltage is applied to the electrodes, negative charges (electrons) are injected from one contact and positive charges (holes) from the other. Some of the opposite charges injected meet up and emit light. The light leaves the device through the lower contact, which is made of the transparent conductive material indium–tin oxide (ITO). The fabrication of such devices is simple: a thin film of the conjugated polymer is deposited on an ITO-coated glass substrate by spin coating, and the top contact is then deposited by evaporation. The spin-coating step involves putting a few drops of polymer solution onto the substrate and then spinning it at high speed. The polymer solution flies off sideways and leaves a uniform thin film of the polymer on the substrate. Hence, although making a uniform thin film of thickness 100 nm might seem difficult, the processing flexibility of polymers means that it can be achieved in a matter of seconds.

Polymer LEDs are very promising for display applications. They offer the prospect of displays that emit light and therefore have excellent visibility, contrast and viewing angle. They can be flat, operate at low voltage, and are relatively simple to

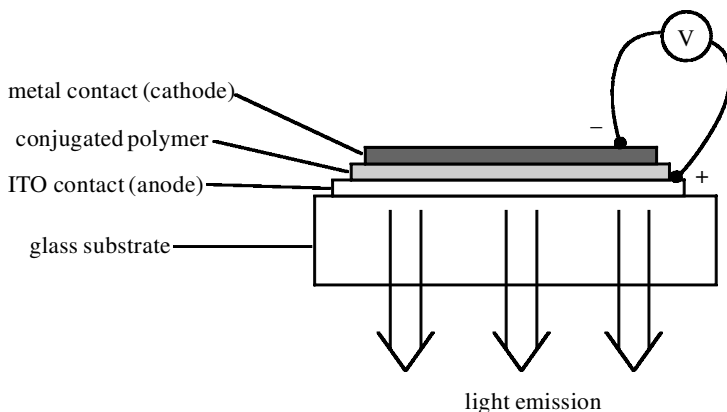


Figure 3. Cross-section of a simple polymer LED. When a voltage is applied, charges are injected into the polymer layer from the contacts, leading to light emission.

manufacture. Further advantages are their fast response (compared with liquid crystals), DC operation, and robustness due to their all-solid-state construction. In the longer term, this technology might be used for very-large-area and even flexible displays. The earliest applications are likely to be backlights for liquid-crystal displays and simple passively addressed displays such as for mobile phones. Two examples of prototype polymer displays are shown in figure 4.

The operation of a polymer LED involves many steps, each with an associated efficiency, as depicted in figure 5. First, opposite charges are injected from the two contacts into the polymer film. Some of these charges will meet and form an excited state called an exciton. Of the excitons formed, it is believed that three-quarters will be in the triplet spin state (which does not emit light) and only one-quarter in the singlet state (which can emit light). Only a fraction of the singlet excitons formed emit light. Finally, only part of the light generated in the polymer layer escapes from the device. The efficiency of an LED can be expressed as the number of photons emitted divided by the number of charges passing through the device. This quantity is known as the external quantum efficiency, and will be denoted Φ_{EL} here. It is determined by the processes described above,

$$\Phi_{\text{EL}} = \Phi_{\text{capture}} \Phi_{\text{spin}} \Phi_{\text{rad}} \Phi_{\text{escape}}, \quad (1.1)$$

where Φ_{capture} is the fraction of opposite charges that meet up to form an exciton, Φ_{spin} is the fraction of excitons formed in the singlet state, Φ_{rad} is the fraction of singlet excitons that emit light, and Φ_{escape} is the fraction of photons generated that escape from the device.

The injection and transport of charge play a vital role in the operation of LEDs. In many early LEDs, the injection of holes (positive charges) was much more efficient than that of electrons (negative charges). This is because in a typical polymer, such as PPV with ITO and aluminium contacts, there is a small energy barrier to the injection of holes at the ITO–polymer interface, and a much larger barrier to the injection of electrons at the metal–polymer interface (see figure 5a). In such devices, many holes pass straight through the structure without meeting an electron, leading to low Φ_{capture} , and low efficiency. The situation can be improved substantially by using an electron-injecting contact with a low work function such as calcium (Braun

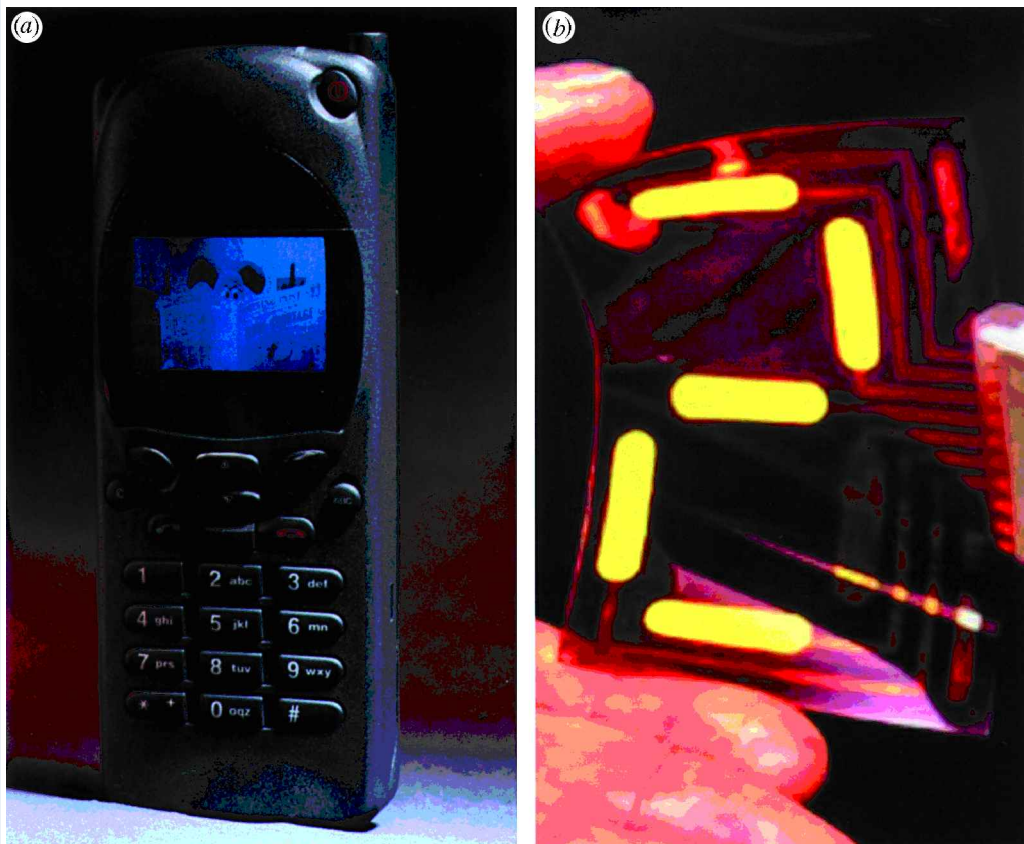


Figure 4. Photograph showing prototype light-emitting polymer displays. (a) A blue polymer display integrated into a mobile phone (courtesy of Cambridge Display Technology Ltd). (b) A flexible-polymer display consisting of seven segments, each of which is a polymer LED (courtesy of Uniux Corporation).

& Heeger 1991). This reduces the energy barrier to the injection of electrons, and, therefore, gives much more balanced injection of electrons and holes. Unfortunately, metals with low work functions are also very reactive, although the situation can be alleviated slightly using alloys such as lithium–aluminium or magnesium–silver. An ingenious alternative is to modify the energy levels of the polymer to facilitate electron injection. This strategy was implemented by making a cyano-substituted PPV with increased electron affinity (Greenham *et al.* 1993; shown in figure 1*d*). Even if the injection of electrons and holes is balanced, their transport may not be. The mobility of electrons is generally much lower than that of holes, and this leads to the opposite charges meeting up close to the metal electrode, which may then quench some of the luminescence.

The polymers used in LEDs must satisfy many criteria, such as being highly luminescent, emitting light of the desired colour, forming good films by spin-coating, and having similar barriers to injection of electrons and holes. It is hard enough to make materials that satisfy these criteria and even harder when the requirement for similar mobilities for electrons and holes is added. An interesting alternative is to make a

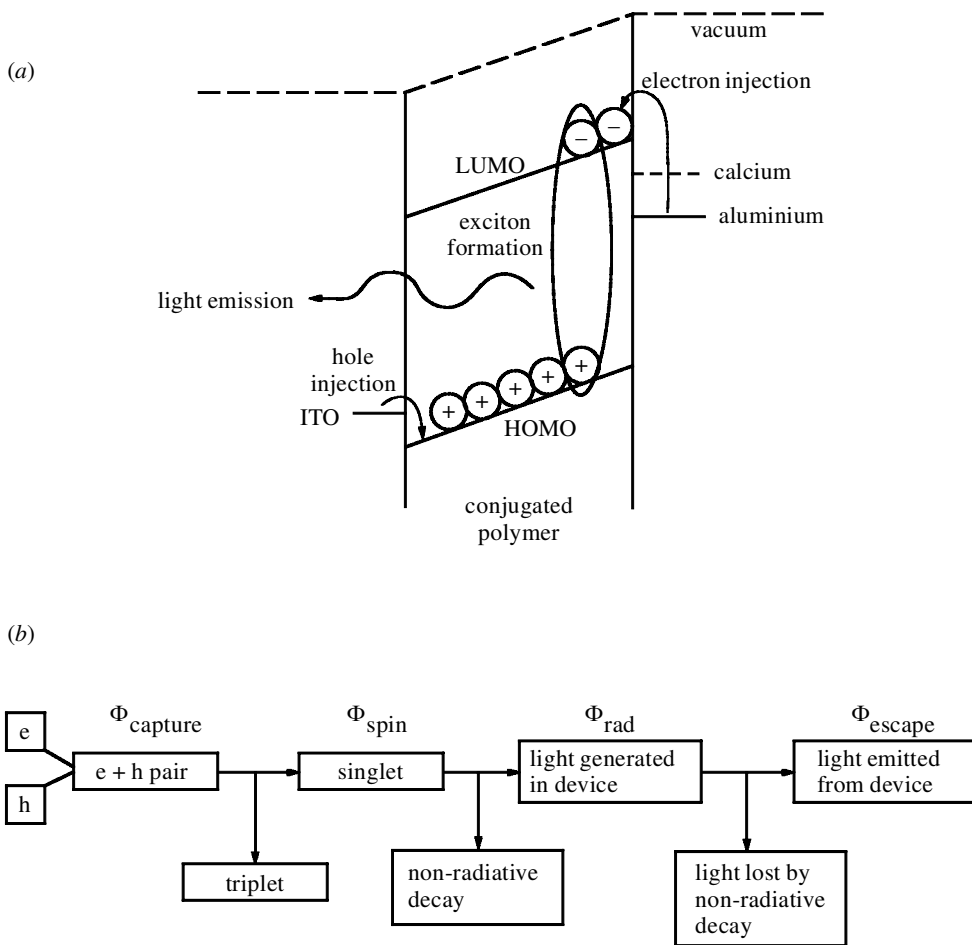


Figure 5. Operation of a polymer LED. (a) Energy levels of an LED under an applied voltage. ‘HOMO’ denotes highest occupied molecular orbital (or valence band). ‘LUMO’ denotes lowest unoccupied molecular orbital (or conduction band). (b) Sequence of events leading from charge injection to light emission.

device with two or more layers of different polymers. One polymer can then be optimized for hole transport and the other for electron transport. This idea builds on the multilayer devices made from small organic molecules (Tang & van Slyke 1987), and inorganic heterostructures. A variety of electron-transporting polymers have been investigated, and these give large improvements over similar devices without the electron-transporting layer. However, there has been recent progress giving efficient devices without the need for a separate electron-transporting layer (Spreitzer *et al.* 1998; Lacey 1998). If this can be achieved for red, green and blue light emission, then simpler device structures may be acceptable.

Light emission from conjugated polymers can also occur when they absorb light. The light-emitting excited state is usually the same whether it is generated electrically or optically. This means that the efficiency of photoluminescence can be used to give an estimate of Φ_{rad} . The value obtained is generally regarded as an upper limit

on Φ_{rad} , because, as mentioned above, if excitons form close to the metal contact of an LED, there are additional quenching mechanisms. Improvements in the synthesis of polymers have increased photoluminescence quantum yields from a few per cent to approaching 100%. The combination of materials and device structures that give balanced injection and transport of electrons and holes together with efficient radiative decay has led to remarkable progress. External quantum efficiencies have increased from 0.001% to more than 10% in only eight years. This improvement of four orders of magnitude in less than a decade represents outstanding progress. The efficiencies of the best devices now exceed those of incandescent light bulbs and many inorganic LEDs. These advances mean that it is now possible to contemplate polymer LEDs for lighting as well as display applications.

What are the prospects for even further increases in efficiency? The answer can be inferred from equation (1.1). In the best devices, Φ_{capture} and Φ_{rad} are approaching 1. Substantial future improvements are therefore likely to come by obtaining light emission from triplets (i.e. increasing Φ_{spin}) or by increasing the fraction of light emitted from the device (i.e. increasing Φ_{escape}). It has recently been shown that energy transfer to a phosphorescent dye can be used to obtain light emission from triplets, and this is a very promising future direction (Baldo *et al.* 1998). There are also ways of increasing the amount of light escaping from a polymer film; for example, by using wavelength-scale microstructure to Bragg scatter waveguided modes out of the film (Matterson *et al.* 2000).

The stability of early polymer LEDs was very poor, and for a long time stability appeared to be a critical issue that could prevent the development of polymer LEDs. Fortunately, the excellent progress in efficiency has been exceeded by advances in device lifetime. The operating lifetime of polymer LEDs has increased from minutes to more than 10 000 h. The main factors leading to this increase are improvements in materials and device fabrication techniques, together with effective encapsulation to keep out oxygen and water. There is still considerable scope for a fuller understanding of device failure mechanisms (Sheats *et al.* 1996), but current lifetimes are acceptable for many commercial applications. A number of excellent reviews give more information about advances in materials and devices for polymer LEDs (Bradley 1996; Burn & Samuel 1998; Feast *et al.* 1996; Friend *et al.* 1992, 1999; Greenham & Friend 1995; Kraft *et al.* 1998; May 1995; Yam 1995). Much work is now being devoted to the challenge of making displays consisting of large numbers of polymer LEDs.

(e) Other polymer devices

In LEDs, the recombination of charges gives light emission. The reverse process, namely absorption of light leading to separation of charges, is also of great interest. It could form the basis of polymer solar cells and photodetectors. The materials and device requirements differ from those of LEDs: in an LED, the aim is to make charges meet up, whereas in photovoltaic devices, the aim is to separate charges. Light absorbed by conjugated polymers leads to the formation of a neutral excited state. In a photovoltaic device, this excited state needs to be split into an electron and a hole, and then the electrons and holes need to be transported to opposite contacts. A very successful way of achieving this is to make a blend of two polymers. It is well known that mixtures of polymers will separate into their different components. This leads to an interpenetrating network of filaments of the two polymers. By choosing

materials with suitable energy levels so that an electron will move into one polymer and a hole into the other, separated charges can be obtained with good efficiency (Halls *et al.* 1995; Yu *et al.* 1995). The separated charges can then be transported through each polymer to the electrodes. This structure can be used in two ways: a bias can be applied and it will then work as a photodiode; alternatively, in the absence of an applied bias, it can be used as a solar cell. Both applications would take advantage of the potential of making large-area devices from polymers. In the case of solar power, there is strong competition from other technologies, but the field of polymer photodetectors is more promising.

The development of a polymer laser is another device target. So far there have been numerous reports of lasing or related phenomena, but they all use optical pumping; in other words, another laser is required to excite the polymer to make it lase. This is a first step towards a polymer laser diode, but there are many obstacles to overcome. In particular, losses associated with metal contacts, injected charges and triplets will need to be overcome to make an electrically pumped laser a realistic proposition.

(f) *Other organic materials*

Polymers are not the only organic semiconductors: there is a wide range of small organic molecules with semiconducting properties. Many of these molecules have been used to make excellent organic devices. For example, the oligomer sexithiophene can be used to make transistors with mobilities approaching those of amorphous silicon. LEDs based on small organic molecules have very good efficiency and lifetime and an impressive colour display has already been made by Pioneer in Japan. More details of these materials are given in the article by Cacialli (this issue) and in a recent review (Kido 1999). A key difference from the polymers is the way in which the small organic molecules are processed. Thin films of these materials are generally deposited by evaporation in a vacuum. This means that in the long term polymers are likely to have advantages for low-cost manufacture (e.g. by printing) and large-area applications.

A potential alternative to either small molecules or polymers is to use conjugated dendrimers (Gebeler *et al.* 1998; Halim *et al.* 1999*a, b*; Burn & Samuel 1998; Moore 1996). The idea is to have a dendritic (highly branched) molecule. The core of the molecule can be chosen to have the desired electronic properties (e.g. colour) and connected by conjugated linkers to the surface groups, which are selected to control the processing properties. Dendritic molecules have been successfully used as charge transport layers and also light-emitting layers in LEDs. Their potential for tuning light-emitting properties has recently been demonstrated in a family of dendrimers with different cores. The resulting molecules were solution processible, and gave light emission in the red, green and blue regions of the spectrum (Halim *et al.* 1999*b*). The key advantage of conjugated dendrimers is that they can combine some of the advantages of small molecules with the solution processing of polymers.

2. Current and future developments

The future of polymer electronics will be shaped by innovations in materials and their processing, guided by understanding of structure–property relations and the operation of devices.

(a) *Designer materials*

A vital part of the rapid development of polymer electronics to date has been the cooperation between chemists and physicists to make improved materials. There is no doubt that this trend will continue and that new developments will be governed by materials innovations. There are two main approaches to improving the properties of semiconducting polymers. The first is largely a 'trial and error' approach in which a chemical modification is made, and its effect then assessed to see whether the material is better or worse. The alternative is to attempt to design a material with desired properties and then synthesize it. It is probably fair to say that both approaches have contributed to the development so far of polymers for LEDs. Clearly, the second approach is desirable, because of the enormous number of possible materials, and the labour involved in making each one. However, it is only possible if there is a detailed understanding of how the properties of a material relate to its structure. This makes a detailed understanding of the physics and chemistry of conjugated polymers vital for their future development.

There are numerous questions that need to be answered and two examples are: what is the nature of the light emitting excited state; and what factors control charge transport in polymer LEDs? Information about the nature of the excited state can be obtained from the spectrum of light emission, the efficiency of light emission, and the lifetime of the excitation once formed (Samuel *et al.* 1997). There has been a lively debate about this in the polymer PPV and its derivatives. In PPV prepared in Cambridge, the results show that the light-emitting excited state resides on a single polymer chain, and it is called the singlet exciton (Greenham *et al.* 1995). In contrast, in other conjugated polymers, including films of a cyano-substituted PPV with high photoluminescence efficiency, the light emission is from an excited state such as an excimer, which is delocalized over two or more neighbouring polymer chains (Jenekhe & Osaheni 1994; Samuel *et al.* 1995; Yan *et al.* 1995). The result is significant because it shows that interaction between molecules must be considered in the design of highly luminescent molecules.

An understanding of the factors controlling charge transport through polymer films is important for the development of materials for device applications. The contacts on a polymer electronic device are typically separated by 100 nm in the case of LEDs and solar cells, and by tens of microns in the case of FETs. It is very unlikely that a single polymer molecule will connect the contacts: instead, charge transport from one contact to the other must involve many hops between neighbouring polymer chains. The ease with which these hops can occur will depend on the arrangement of the polymer chains, and, hence, also on the interactions between polymer molecules.

The picture that is emerging is that it is not simply the chemical structure of the polymers that is important but also the way the molecules pack together: the morphology of the sample. The morphology of the sample is ultimately determined by the chemical composition of the polymer and the processing used. However, large parts of conjugated polymer films are often amorphous, making it difficult to obtain information about chain packing by structural techniques such as X-ray scattering, which are better suited to crystalline materials. Finding ways of processing conjugated polymers and even using processing to control properties will be important. For example, charge-carrier mobilities could be improved by increasing the order of the samples by using very regular molecular structures, stretch orientation, or liquid-crystal phases.

There have been some notable successes of rational design of materials with desired properties. As mentioned earlier, one example is the use of a cyano-substitution on PPV to increase its electron affinity, thereby facilitating electron injection and transport (Greenham *et al.* 1993). Another example is the use of the ethyl-hexyloxy sidegroup to make the soluble polymer MEH-PPV (see figure 1e; see also Wudl & Hoger 1991). The asymmetrical substitution impedes crystallization of the polymer making it more soluble. A further example is tuning colour by making copolymers of two different materials to tune from the colour of one to the colour of the other (Burn *et al.* 1992). This trend will continue and future developments in relating the properties of conjugated polymers to their structure and morphology will mean that more and more materials can be designed with desired properties.

However, it is not enough simply to know what structure would be an ideal material, it is necessary to be able to make it. For example, we know that impurities that quench luminescence are bad for LEDs, but it is much harder to ensure that there are none. Developments in chemistry will be another vital part of the development of polymer electronics. Current improvements in synthesis are giving improvements in purity, control of end groups, and control of molecular weight. By changing sidegroups, morphology and solubility can be controlled, allowing control of charge transport and processing. An important distinction from some areas of synthetic chemistry is that exceptionally high purity is needed. An impurity that quenches luminescence at a concentration of one part per million could cause a significant reduction in the efficiency of an LED. One promising direction is ring-opening metathesis polymerization, because it gives control over molecular weight and a narrow distribution of molecular weights (Feast *et al.* 1996; Knoll & Schrock 1989; Swager *et al.* 1988).

In the longer term, new approaches to the synthesis of polymeric electronic materials will develop. At present, many organic LEDs have several layers, each separately deposited and adapted for a particular function (e.g. light emission, electron transport, hole transport). A preferable architecture would be to have single molecules extending from contact to contact, and molecules consisting of different sections adapted to different functions. This idea is illustrated in figure 6 for the example of an LED. The part of the molecule near the hole-injecting contact would have a chemical composition suited for transporting holes to a central section adapted for light emission, while the other end of the molecule conveys electrons to the light-emitting region. Ideally, the molecules would be highly ordered to allow efficient charge transport, and give a film with high physical robustness. A further development of this idea would be to incorporate segments of conducting polymers on each end of the molecule instead of conducting contacts. Even better would be if each section of the molecule were designed to associate with similar sections of other molecules. This could mean that if the molecules were mixed together in solution, then they would associate to form a light-emitting polymer layer. Such an architecture would open endless possibilities of tuning properties: by changing repeat units, mixing different repeat units, changing the length of segments, or even having a continuous gradation of properties rather than discrete segments.

While the idea above is at present a dream, some of the ingredients required are already discernible. The rapidly developing area of supramolecular chemistry is concerned with assemblies of molecules and interactions between molecules, linking to the theme of morphology discussed earlier. Attempts have been made to make molecular wires and even molecular diodes. A promising approach is the use of 'self-

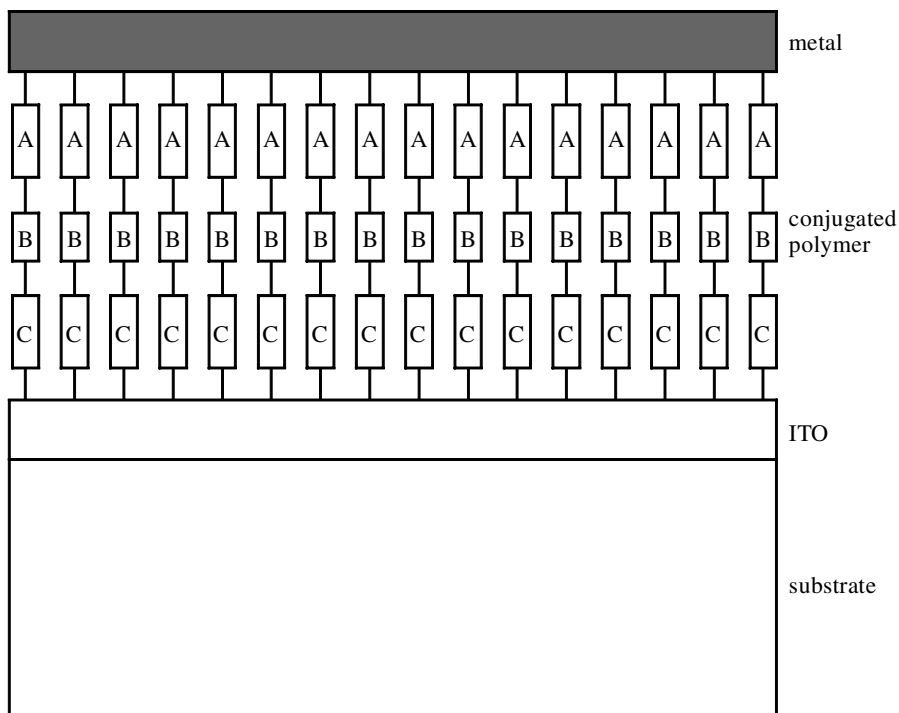


Figure 6. Possible future design of an LED in which ordered single molecules connect the contacts. Each molecule combines electron-transporting (A), light-emitting (B), and hole-transporting (C) functions.

assembly' techniques, in which a structure is built up by depositing successive layers of molecules in such a way that there is a chemical bond between each successive layer. LEDs made in this way have been demonstrated (Baur *et al.* 1998).

The control of order is widely recognized to be important. A possible future approach is to use a template such as a system of nanotubes formed in a liquid-crystal mesophase of silica. These could be used to make an array of straight conjugated polymer molecules. Alternatively, a suitable rigid conjugated polymer might be developed that could form such a mesophase itself without the need for a silica template.

Once again we return to the theme of needing ways of making molecules suitable for the ideas outlined above. We would like a way of making any desired sequence of monomer units to give a polymer with particular properties. This may sound far-fetched but it is already prevalent in the area of molecular biology, where desired sequences of nucleotides and amino acids are commercially available. The same facility would revolutionize polymer science. The seeds of such an approach are emerging: the solid phase synthesis of thiophene and other oligomers using an approach inspired by Merrifield (1963) has recently been reported (Jones *et al.* 1997; Malenfant & Frechet 1998). The impact of precise control over structures is evident in the field of inorganic semiconductors, where molecular beam epitaxy and chemical vapour deposition have given exquisite control of material properties.

(b) *Flexible electronics*

A very exciting aspect of polymer electronics is the possibility of building flexible electronic circuits by depositing polymer layers on suitable flexible substrates. Perhaps the first question to consider in this context is whether anybody would want flexible electronics, and in some ways this is a test of imagination. In the context of displays, one significant use of flexibility would be to allow a particular shape of display to be realized. For example, some displays (e.g. car dashboards) are curved, allowing optimal use of space and helping to keep off stray light. For some of these applications, there is no need to change the shape of the display once it has been fitted, but flexibility would provide a convenient way of realizing a particular shape. However, there could also be uses for flexible displays; for example, they could easily be stored by folding (or rolling) them up when they are not in use. In the context of electronics, smart cards that contain a simple chip and electronic bar-codes are growing in use. It is desirable for such devices to be flexible, and polymer FETs provide a possible way of achieving this (Brown *et al.* 1995; de Leeuw 1999).

However, there are two additional implications of flexibility that go far beyond the uses described above. The first is that flexibility confers robustness. An ability to bend means that brittle fracture can be avoided. This is relevant to all applications, but especially to those involving very-large-area devices. For example, a display panel of dimensions of a few metres would be extremely vulnerable to breakage unless it were flexible or had a very cumbersome support. The other important implication is that flexibility dramatically enhances manufacturability. It opens the possibility of having a process that begins with a drum of substrate that is then coated with appropriate polymer layers, and then finally sliced into polymer electronic devices in a single continuous process.

An excellent demonstration of the feasibility of flexible polymer LEDs was made by Gustafsson *et al.* (1992), and this has subsequently been developed into the device shown in figure 4b. These devices are made on a poly(ethylene terephthalate) substrate (as used for transparencies for overhead projectors) coated with conducting polyaniline as a hole-injecting contact. A semiconducting polymer layer is deposited on top of this, and the device is completed by a top contact of calcium. As can be seen in the figure, the device can be bent and it still operates perfectly. Philips has demonstrated flexible electronic tags. Flexibility could be useful in the future for lighting applications. Existing light sources are generally very bright over a very small area (e.g. the filament of an incandescent lamp). A very-large-area light-emitting polymer device could be used to give a very different and perhaps more restful illumination in which low brightness over a large area is used. Flexibility could also be exploited to make light-emitting clothing for safety or fashion applications.

A major disadvantage of using polymer substrates is that they are far more permeable to air and water than glass, which is more commonly used as a substrate (May 1996). This is a problem because oxygen and water cause degradation of polymer devices. There are two main approaches to dealing with this problem: the first is to find or design substrate materials with improved barrier properties; the second is to develop conjugated polymers that are more resistant to air and water.

(c) *Printable electronics*

Advances in polymer processing will play an important role in the development of polymer electronics. Printing is the most exciting area because it really exploits the favourable polymer processing properties mentioned in §1. The greatest advantage of printing is its potential for mass production and patterning. It could be used to define contacts for pixellated displays or simply to define the shape of a light-emitting company logo. In addition, it is an additive process and therefore minimizes wastage of material. Some forms of printing would also be well suited to rapid prototyping or small-scale customized production, while other forms could allow mass production.

Progress in printing polymer electronics is very encouraging. Yang and co-workers have demonstrated ink-jet printing of polymer LEDs (Bharathan & Yang 1998). Meanwhile, it has been shown that FETs can be printed with respectable charge-carrier mobilities (Bao *et al.* 1997; Garnier *et al.* 1994). Even more impressive is the demonstration of a prototype miniature television screen 50 mm² square and 2 mm thick. It results from the alliance between Cambridge Display Technology and Seiko-Epson, and was made by ink-jet printing of polymers onto polysilicon thin-film transistors. The prototype is yellow-green and the companies are now working towards a full-colour version of the display.

In future, we can expect to see a dramatic increase in the use of printing for the fabrication of polymer electronic circuits. One area of particular interest would be to combine FETs and LEDs to make an actively addressed polymer display. There are many technical challenges to achieving this, but the possibility of combining these devices in structures made by spin coating has recently been demonstrated (Dodabalapur *et al.* 1998; Siringhaus *et al.* 1998).

As printing develops, we can expect to see it move towards higher and higher speed. Basic lithographic printing presses can achieve 10 000 impressions per hour. A significant development by Harrison and co-workers (Ramsey *et al.* 1997) has been a conducting ink compatible with lithographic printing. The ink consists of conducting metal particles in a polymer matrix. It enables conductive circuits to be printed at very high speed. The conventional process for making 'printed' circuits involves a photographic exposure followed by etching, which generates acid waste. The lithographic printing approach is dramatically faster and cleaner. If it can be used to print polymer electronic devices, it would allow electronics fabrication at unprecedented speed and low cost. This could transform the range of applications of electronics.

3. Outlook

The impact of materials is so great that eras of history are named after them. In the modern age, improvements in materials have transformed our lives with developments from jet engines to skyscrapers. In this article we have seen how conducting and semiconducting polymers are opening new directions in electronics and polymer science. The development of polymer LEDs from discovery to the point of commercial manufacture in a decade is remarkably fast compared with other areas of semiconductor electronics. Simple polymer displays, such as passively addressed displays for mobile phones or backlights for liquid-crystal displays, are poised to enter the marketplace. The subsequent development of the field will depend as much on

commercial as on technical issues. Assuming the early displays are successful, we can expect to see colour displays with increasing information content.

In the longer term, applications that make the maximum use of polymer-processing properties are very significant. The scope for flexible electronics and very-large-area displays is very exciting. Even more significant is the possibility of printing electronics. Beyond that it is possible to envisage combining many devices onto a single sheet of plastic so that display, logic, light detection and even power generation are all integrated. The technical challenges should not be underestimated, but nor should the potential rewards.

The potential of this field is so great that it has only been possible to select a few aspects of it in this article. Numerous opportunities exist at the boundaries with other research fields. For example, there is a healthy symbiosis with the field of quantum optics: luminescent polymers can be used to make novel photonic structures, and, conversely, photonic structures can be used to control the properties of polymers, including lasing. There is also the potential for hybrid devices combining organic and inorganic materials; the compatibility of semiconducting polymers with silicon is an attractive feature. Equally exciting is the scope for polymer electronics to inspire new chemistry, and for new physics to emerge from the new materials and devices.

It is a pleasure to acknowledge the support of the Royal Society through a University Research Fellowship. Additional financial support was provided by the EPSRC Electronic Materials for Displays, and Electronic Product Design and Manufacture initiatives. I am grateful to G. Rumbles and J. M. Lupton for reading the manuscript.

References

- Baldo, M. A., O'Brien, D., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E. & Forrest, S. 1998 Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* **395**, 151–154.
- Bao, Z., Feng, Y., Dodabalapur, A., Raju, V. R. & Lovinger, A. J. 1997 High-performance plastic transistors fabricated by printing techniques. *Chem. Mater.* **9**, 1299–1301.
- Barker, P. S., Petty, M. C., Monkman, A. P., McMurdo, J., Cook, M. J. & Pride, R. 1996 A hybrid phthalocyanine/silicon field-effect transistor sensor for NO₂. *Thin Solid Films* **285**, 94–97.
- Baur, J., Kim, S., Balanda, P., Reynolds, J. & Rubner, M. 1998 Thin-film light-emitting devices based on sequentially adsorbed multilayers of water-soluble poly(*p*-phenylene)s. *Adv. Mater.* **10**, 1452–1455.
- Bharathan, J. & Yang, Y. 1998 Polymer electroluminescent devices processed by inkjet printing. I. Polymer light-emitting logo. *Appl. Phys. Lett.* **72**, 2660–2662.
- Bradley, D. D. C. 1996 Electroluminescent polymers: materials, physics and device engineering. *Curr. Op. Solid State Mater. Sci.* **1**, 789–797.
- Braun, D. & Heeger, A. J. 1991 Visible light emission from semiconducting polymer diodes. *Appl. Phys. Lett.* **58**, 1982–1984.
- Brown, A. R., Pomp, A., Hart, C. M. & Deleeuw, D. M. 1995 Logic gates made from polymer transistors and their use in ring oscillators. *Science* **270**, 972–974.
- Burn, P. L. & Samuel, I. D. W. 1998 Light-emitting polymers—the shape of things to come? *Materials Today* **1**, 3–5.
- Burn, P. L., Holmes, A. B., Kraft, A., Bradley, D. D. C., Brown, A. R., Friend, R. H. & Gymer, R. W. 1992 Chemical tuning of electroluminescent copolymers to improve emission efficiencies and allow patterning. *Nature* **356**, 47–49.

- Burroughes, J. H., Jones, C. A. & Friend, R. H. 1988 Polymer diodes and transistors: new semiconductor device physics. *Nature* **335**, 137–141.
- Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L. & Holmes, A. B. 1990 Light-emitting diodes based on conjugated polymers. *Nature* **347**, 539–541.
- Cao, Y., Smith, P. & Heeger, A. J. 1992 Conterion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers. *Synth. Met.* **48**, 91–97.
- Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., Gau, S. C. & MacDiarmid, A. G. 1977 Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.* **39**, 1098–1101.
- de Leeuw, D. 1999 Plastic electronics. *Physics World* **12** (March), 31–34.
- Dodabalapur, A., Bao, Z., Makhija, A., Laquidano, J. G., Raju, V. R., Feng, Y., Katz, H. E. & Rogers, J. 1998 Organic smart pixels. *Appl. Phys. Lett.* **73**, 142–144.
- Feast, W. J., Tsibouklis, J., Pouwer, K. L., Groenendaal, L. & Meijer, E. W. 1996 Synthesis, processing and material properties of conjugated polymers. *Polymer* **37**, 5017–5047.
- Friend, R. H., Bradley, D. D. C. & Holmes, A. B. 1992 Polymer light-emitting diodes. *Physics World* (November), p. 42.
- Friend, R. H. (and 10 others) 1999 Electroluminescence in conjugated polymers. *Nature* **397**, 121–127.
- Garnier, F., Hajlaoui, R., Yassar, A. & Srivastava, P. 1994 All-polymer field-effect transistor realised by printing techniques. *Science* **265**, 1684–1686.
- Gebeler, C., Antoniadis, H., Bradley, D. & Shirota, Y. 1998 Space-charge-limited charge injection from indium tin oxide into a starburst amine and its implications for organic light-emitting diodes. *Appl. Phys. Lett.* **72**, 2448–2450.
- Greenham, N. C. & Friend, R. H. 1995 Semiconductor device physics of conjugated polymers. *Solid State Phys.* **49**, 1–149.
- Greenham, N. C., Moratti, S. C., Bradley, D. D. C., Friend, R. H. & Holmes, A. B. 1993 Efficient polymer-based light-emitting diodes based on polymers with high electron affinities. *Nature* **365**, 628–630.
- Greenham, N. C., Samuel, I. D. W., Hayes, G. R., Phillips, R. T., Kessener, Y. A. R. R., Moratti, S. C., Holmes, A. B. & Friend, R. H. 1995 Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers. *Chem. Phys. Lett.* **241**, 89–96.
- Gustafsson, G., Cao, Y., Treacy, G., Klavetter, F., Colaneri, N. & Heeger, A. 1992 Flexible light-emitting-diodes made from soluble conducting polymers. *Nature* **357**, 477–479.
- Halim, M., Pillow, J. N. G., Samuel, I. D. W. & Burn, P. L. 1999a Conjugated dendrimers for light-emitting diodes: effect of generation. *Adv. Mater.* **11**, 371–374.
- Halim, M., Samuel, I. D. W., Pillow, J. N. G. & Burn, P. L. 1999b Conjugated dendrimers for LEDs: control of colour. *Synth. Met.* **102**, 1468–1469.
- Halls, J. J. M., Walsh, C. A., Greenham, N. C., Marseglia, E. A., Friend, R. H., Moratti, S. C. & Holmes, A. B. 1995 Efficient photodiodes from interpenetrating polymer networks. *Nature* **376**, 498–500.
- Jenekhe, S. A. & Osaheni, J. A. 1994 Excimers and exciplexes of conjugated polymers. *Science* **265**, 765–768.
- Jones, L., Schumm, J. S. & Tour, J. M. 1997 *J. Org. Chem.* **62**, 1388.
- Kido, J. 1999 Organic displays. *Physics World* **12** (March), 27–30.
- Knoll, K. & Schrock, R. R. 1989 Preparation of tert-butyl-capped polyenes containing up to 15 double bonds. *J. Am. Chem. Soc.* **111**, 7989–8004.
- Kraft, A., Grimsdale, A. C. & Holmes, A. B. 1998 Electroluminescent conjugated polymers—seeing polymers in a new light. *Angew. Chem. Int. Ed.* **37**, 402–428.
- Lacey, D. 1998 High-efficiency polymer light-emitting diodes. In *9th Int. Workshop on Organic and Inorganic Electroluminescence, Oregon, USA*.

- Malenfrant, P. R. L. & Frechet, J. M. J. 1998 The first solid-phase synthesis of oligothiophenes. *Chem. Commun.*, pp. 2657–2658.
- Matterson, B. J., Salt, M. G., Barnes, W. L. & Samuel, I. D. W. 2000 Effect of lateral microstructure on conjugated polymer luminescence. (Submitted.)
- May, P. 1995 Polymer electronics—fact or fantasy? *Physics World* (March), 52–57.
- May, P. 1996 Light-emitting polymers—technology for conformable graphic displays. In *Society for Information Display Meeting, San Diego, May*.
- Merrifield, R. B. 1963 *J. Am. Chem. Soc.* **85**, 2149.
- Moore, J. 1996 Molecular architecture and supramolecular chemistry. *Curr. Op. Solid State Mater. Sci.* **1**, 777–788.
- Ramsey, B., Evans, P. & Harrison, D. 1997 A novel circuit fabrication technique using offset lithography. *J. Elec. Manuf.* **7**, 63–67.
- Samuel, I. D. W., Rumbles, G. & Collison, C. J. 1995 Efficient interchain photoluminescence in a high-electron-affinity conjugated polymer. *Phys. Rev. B* **52**, 11 573–11 576.
- Samuel, I. D. W., Rumbles, G. & Friend, R. H. 1997 Luminescence efficiency and time-dependence: insights into the nature of the emitting species in conjugated polymers. In *Primary photoexcitations in conjugated polymers: molecular exciton versus semiconductor band model* (ed. N. S. Sariciftci), pp. 140–173. World Scientific.
- Sheats, J. R., Antoniadis, H., Hueschen, M., Leonard, W., Miller, J., Moon, R., Roitman, D. & Stocking, A. 1996 Organic electroluminescent devices. *Science* **273**, 884–888.
- Sirringhaus, H., Tessler, N. & Friend, R. H. 1998 Integrated optoelectronic circuits based on conjugated polymers. *Science* **280**, 1741–1744.
- Spreitzer, H., Becker, H., Kluge, E., Kreuder, W., Schenk, H., Demandt, R. & Schoo, H. 1998 Soluble phenyl-substituted PPVs—new materials for highly efficient polymer LEDs. *Adv. Mater.* **10**, 1340–1344.
- Swager, T. M., Dougherty, D. A. & Grubbs, R. H. 1988 Strained rings as a source of unsaturation—polybenzvalene, a new soluble polyacetylene precursor. *J. Am. Chem. Soc.* **110**, 2973–2974.
- Tang, C. W. & van Slyke, S. A. 1987 Organic electroluminescent diodes. *Appl. Phys. Lett.* **51**, 913–915.
- Wudl, F. & Hoger, S. 1991 PCT patent application WO94/20589.
- Yam, P. 1995 Plastics get wired. *Scientific American* (July), 74–79.
- Yan, M., Rothberg, L. J., Kwock, E. W. & Miller, T. M. 1995 Interchain excitations in conjugated polymers. *Phys. Rev. Lett.* **75**, 1992–1995.
- Yu, G., Gao, J., Hummelen, J. C., Wudl, F. & Heeger, A. J. 1995 Polymer photovoltaic cells—enhanced efficiencies via a network of internal donor–acceptor heterojunctions. *Science* **270**, 1789–1791.

AUTHOR PROFILE

I. D. W. Samuel

Born in London, Ifor Samuel read Natural Sciences at Cambridge, graduating in 1988. He remained there for his PhD on femtosecond spectroscopy of conjugated polymers, and was elected a Fellow of Christ's College in 1991. He spent two years at CNET-France Telecom in Paris working on nonlinear optics of organic materials. He moved to Durham in 1995 to set up a research group on light-emitting polymers. His current research involves the use of optical and electrical spectroscopy to study these materials with the aim of understanding and improving them. Aged 32, he is a Royal Society University Research Fellow. His other interests include music, theatre, travelling and hill-walking.

