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Organic semiconductors for the new millennium

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Organic semiconductors are carbon-based materials capable of transporting charged excitations and interacting with visible radiation. For this reason they can replace conventional inorganic semiconductors in optoelectronic devices such as light-emitting diodes, photovoltaic cells and field-effect transistors. Organic chemistry offers a wide variety of tools for tailoring the functional properties of these materials, essentially molecular and macromolecular in nature, via addition or substitution of carefully designed chemical groups. This also provides the opportunity for transduction of chemical or biochemical interactions into optoelectronic signals, and hence for the fabrication of chemo- and bio-sensors. Very cheap manufacture, the possibility of covering large-area and flexible substrates with an immense freedom in the tunability of the electronic and optical properties are the promise of organic, possibly polymeric, optoelectronics for the next millennium. In this paper we briefly review some aspects of the basic physics and give an account of the state-of-the-art reached so far in turning these materials into useful devices. Finally, we attempt to project how the development of the latter may link up to progress in the biotechnologies.

Keywords: semiconductors; organics; optoelectronics; conjugated molecules; polymers; π-electrons

1. Organic semiconductors: a 'soft interface' between chemistry and solid state physics

In the last 50 years, inorganic semiconductors have offered an interesting ground for investigation of the physics of the solid state and also for the development of optoelectronic devices for the treatment of information, which are now leading the transition to a post-industrial society based on information technology. So far, optoelectronics has been dominated by inorganic materials (germanium, silicon, gallium arsenide, or other III/V or II/VI compounds) with organics basically relegated to the role of insulators. In the last 20 years, however, conjugated molecules, and macromolecules in particular,† have been proposed as a novel class of semiconductors with technological potential for the treatment of information. These carbon-based materials offer a unique opportunity for looking at a different physics, largely dominated by the formation of a partly delocalized π-orbital.

The latter originates from the lateral overlap of the p_z orbitals of adjacent, sp^2 hybridized carbon atoms, as schematically depicted in figure 1.

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† In what follows we will often refer explicitly to polymers, although short oligomers often share the same or similar properties. This is because we consider that conjugated polymers are more promising for optoelectronics applications.

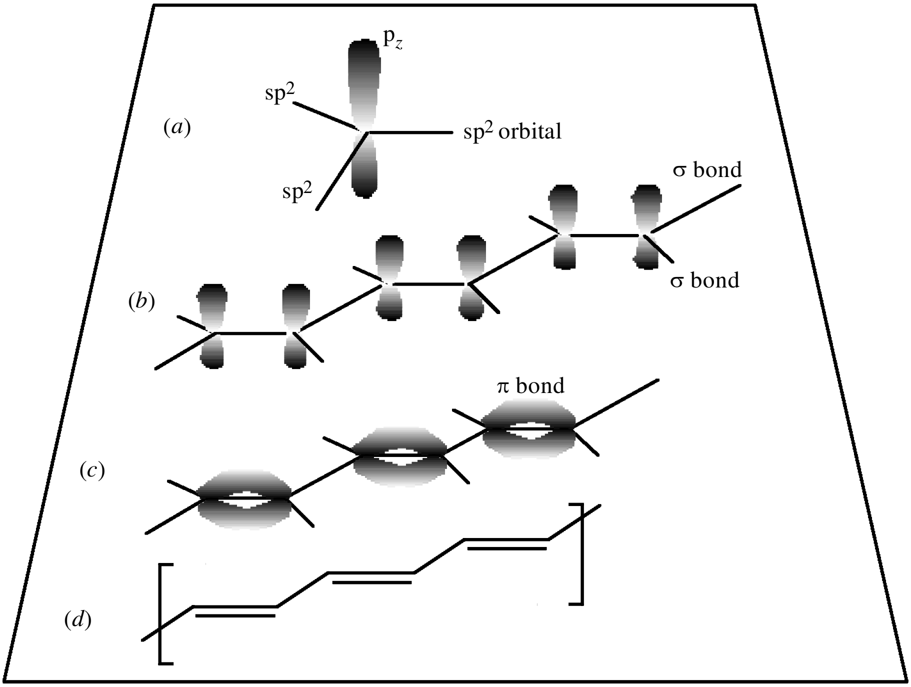

Figure 1. (*a*) Schematic representation of sp^2 hybridized C atoms (lines) and of the non-hybridized p$_z$ orbital. (*b*) Adjacent carbon atoms linked by the sigma bonds originating from the sp^2 orbitals. (*c*) Lateral overlap of the p$_z$ orbitals from adjacent carbons forms one π bond every two carbons. (*d*) The conjugated structure of polyacetylene.

The materials formed in this way are called 'conjugated' because, in addition to the sigma bonds, there is one π-bond every two carbon atoms (see figure 1*c*). Note that the whole structure is rationalized in terms of alternating single and double bonds as in polyacetylene (figure 1*d*), although the π-electron wave function extends over both (nominally) single and double bonds. Indeed, it would be more appropriate to describe it in terms of a charge density wave. The presence of a π-electron system introduces remarkable differences with respect to sigma-bonded (macro)molecules, since it is responsible for a low value of the redox potentials (i.e. of the electric potentials required for oxidation or reduction of the materials), for small energy gaps (in the visible region), and also for an intrachain mobility of up to 0.1 cm^2 V^{-1} s^{-1}, as recently measured by Hoofmann *et al.* (1998). The low redox potentials allow easy 'doping' by charge transfer from electron-withdrawing or donating species, such as iodine (Chiang *et al.* 1977), oxygen, or calcium (Bröms *et al.* 1995). This provides the possibility of modulating the carrier concentrations. The occurrence of the energy gap in the visible range is also very important, as it makes these materials suitable for a number of optoelectronic applications such as light-emitting diodes (LEDs), graphic displays, and photovoltaic (PV) cells.

In the case of linear polymers, which often include aromatic rings as in poly(*p*-phenylene vinylene), PPV, and analogues (see figure 2), the π-orbital develops along the chain, with an intrinsic one-dimensional (1D) character, and subsequent lateral

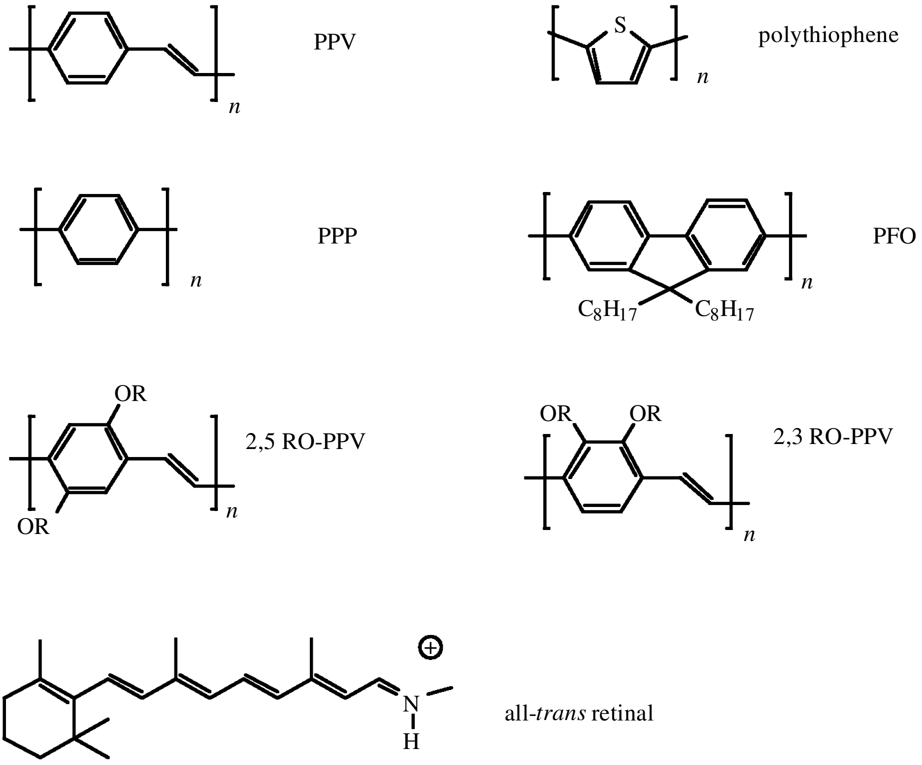

Figure 2. The chemical structure of poly(*p*-phenylene vinylene), PPV, poly(*p*-phenylene), PPP, polythiophene, poly(9,9-dioctylfluorene), PFO, and of PPV derivatives which have been functionalized with alkoxy chains in different positions of the benzylic moiety. The side chains provide solubility and also allow for tuning of the molecule geometry and electronic properties. Also shown is the all-*trans* retinal, a molecule involved in visual bio-processes.

confinement of the wave function. The effective delocalization of the orbital or 'conjugation', however, does not extend for the whole polymer chain, being interrupted by morphological defects, such as kinks and twists of the chain, or chemical defects, such as sp^3 carbons, carbonyl moieties, *cis* linkages, or substitutions which limit the extent of the electron (or hole) wave function. Polymers are then, by their very nature, disordered materials, containing conjugated segments of different lengths, and hence have different electronic properties. In addition, the 1D character of the π-orbital is often reduced in the solid state or in solutions prepared with poor solvents, where the molecules' close proximity may favour the formation of relatively extended interchain excitations such as aggregates, in the ground state, or excimers, in the excited state (Hayes *et al.* 1995*a*). Further spatial confinement of the excitations arises, however, from self-localization induced by geometric relaxation of the soft polymeric chains, and from electron correlation. For these reasons the excited states can be regarded as electron–hole pairs, or excitons, with substantial binding energies, in the range 0.2–1 eV.

The importance of both structural relaxation and electron–electron interactions has been elucidated extensively with the help of quantum chemical calculations,

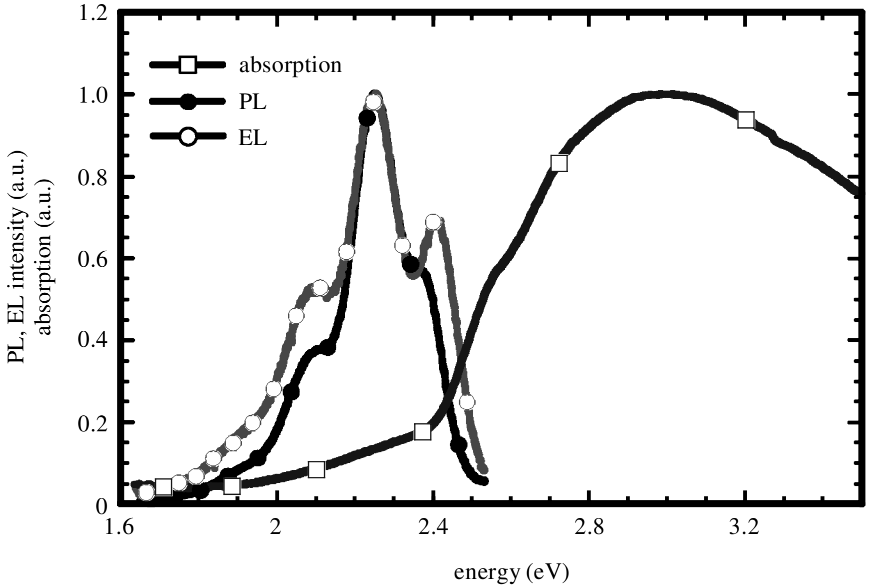

Figure 3. Absorption and emission spectra for poly(*p*-phenylene vinylene), PPV. Absorption and photoluminescence are from a thin film on Spectrosil, whereas the electroluminescence is from a single layer cell with indium tin oxide and Al electrodes.

which have proved very successful, especially in combination with photoelectron spectroscopies, in the modelling of the energetic structure (Salaneck *et al.* 1996).

Experimentally, the presence of geometric relaxation can be inferred from analysis of the optical properties, after excluding the effects of the exciton migration through the disordered density of states that characterizes the electronic structure of the materials, as discussed in more detail later on. This migration process can lead to a significant shift between the optical absorption and the emission spectra (figure 3), and can be eliminated by exciting the photoluminescence (PL) with a radiation of low energy. Below a certain energy threshold ('localization threshold'), in fact, only few molecules with a long conjugation can absorb the radiation, and energy migration is impossible for lack of lower energy sites in their vicinity. The relative importance of disorder and geometrical relaxation in determining the red-shift depends very much on the details of the geometry and of the electronic structure of the semiconductor. For PPV for example, the PL red-shift is almost totally dominated by the energy migration process, whereas for the phenylated derivative poly(4,4′-diphenylene diphenylvinylene), PDPV, the intrinsic Stokes shift, i.e. due to the geometric relaxation, is very significant. Electron–phonon coupling is especially apparent as a progression of peaks in the luminescence spectra, referred to as 'vibronic structure'. As mentioned above, there is now a large consensus regarding a relatively high binding energy (greater than 0.2 eV) of the electron–hole pairs (excitons), which can be generated by absorption of a photon or by injection and subsequent mutual capture of hole-like and electron-like carriers (Rauscher *et al.* 1990). Note that the presence of charge on a polymeric chain also determines an alteration of the geometry, and the carriers are then called positive or negative 'polarons', by analogy with the charge carriers in polar crystals, which are accompanied by a

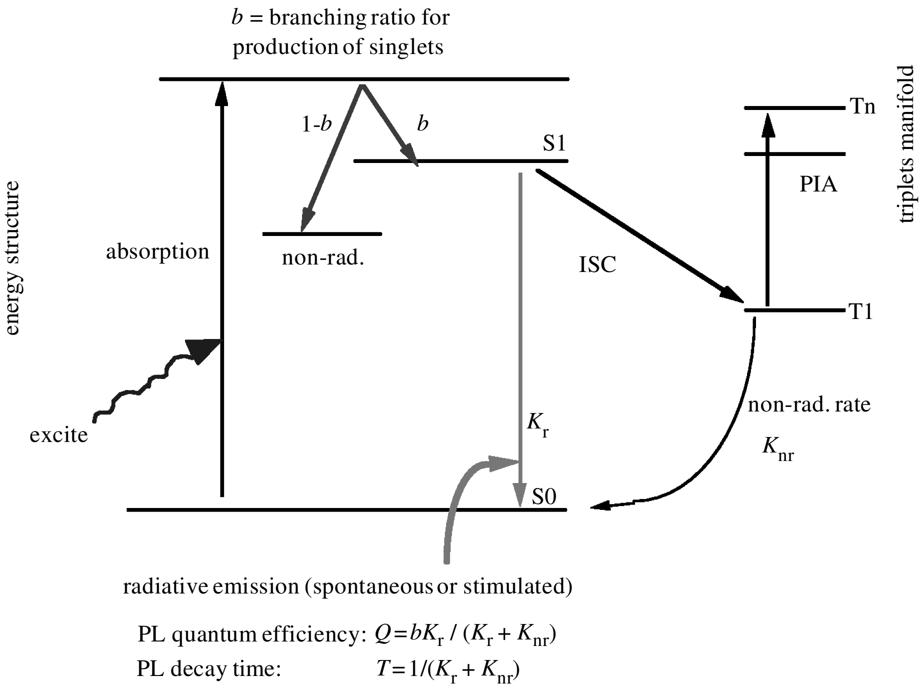

Figure 4. Typical radiative and non-radiative transitions in a conjugated semiconductor such as PPV.

distortion, or ‘polarization’ of the lattice. The typical radiative and non-radiative transitions in a conjugated semiconductor are summarized in figure 4.

Excitation at energies above the absorption edge creates singlet states (spin = 0), which rapidly thermalize, reaching the lowest vibrational level in the first electronic excited state (S1), or other non-radiative states, possibly charged polaron pairs (Yan *et al.* 1994). The thermalization happens in less than 200–400 fs (Hayes *et al.* 1995*b*; Lemmer *et al.* 1993), whereas the experimental radiative decay time of singlets for a polymer such as PPV is of the order of 300 fs. In view of a PL efficiency of *ca.* 30%, this implies, following a classical Strickler–Berg analysis (Strickler & Berg 1962), an intrinsic lifetime of the order of 1–1.2 ns, which is thought to be common to a large number of conjugated chromophores (Greenham & Friend 1995; Greenham *et al.* 1995). Equations (1.1) summarize the relationship between fluorescence efficiency (Φ), and radiative (τ_{rad}^{-1}), non-radiative ($\tau_{\text{non-rad}}^{-1}$), and measured unimolecular luminescence (τ_{lum}^{-1}) decay rates:

$$\Phi = b\frac{\tau_{\mathrm{rad}}^{-1}}{\tau_{\mathrm{lum}}^{-1}}, \qquad \tau_{\mathrm{lum}}^{-1} = \tau_{\mathrm{rad}}^{-1} + \tau_{\text{non-rad}}^{-1}. \tag{1.1}$$

Here b is the so-called branching ratio, i.e. the portion of the photogenerated excitations that produces emissive singlet excitons (Yan *et al.* 1994). Harrison *et al.* (1996) have shown that b is independent of the excitation energy and almost unity for non-oxidized PPV from the precursor route, but less than unity for oxidized PPV. Similarly, it can be expected that aggregation effects, typical of other semiconductors that also suffer from concentration quenching of the luminescence, are likely to reduce the value of b.

As is apparent in figure 3 the photoluminescence and the electroluminescence are extremely similar, with differences only in the relative height of the different vibronic peaks, arising from a combination of interference and self-absorption effects. This justifies the identification of the EL radiative species as singlets.

In addition to polaron pair formation, one of the most important non-radiative channels available for quenching of the luminescence is intersystem crossing (ISC) from the singlet to the triplet manifold. Triplets are non-luminescent in PPV and most other polymers unless the radiative transition (phosphorescence) is made 'less forbidden' by partial relaxation of the spin selection rule, due to substantial spin-orbit coupling, which in turn can be introduced by the presence of a heavy atom such as Pt or Pd. This may increase substantially the phosphorescence yield, and it is very interesting for electroluminescent processes (Baldo *et al*. 1998; Cleave *et al*. 1999), as we shall discuss in detail in the application section, since triplet production in LEDs may be three times as large as that of singlets, on the basis of spin statistics for recombination of an electron and hole, both of arbitrary spin orientation, if probability of exciton formation is the same for singlets and triplets (Shuai *et al*. 2000).

Although stimulated emission in conjugated dyes in solution has been known for a number of years, lasing in solid thin films of undiluted conjugated polymers has been reported only recently (Tessler *et al*. 1996). This is probably due to the substantial improvements in the chemical design, synthesis and purification of the semiconductors, and hence in the high values of the absolute PL efficiency (by now between 60 and 80% in solid state). Spectral overlaps between the PL and absorptions in the triplet manifold or by charged species are significant (Tessler *et al*. 1998), and lead to relatively high excitation thresholds (greater than 120 nJ cm^{-2}, equivalent to an exciton concentration of $2 \times 10^{17}\ \mathrm{cm}^{-3}$ (Granlund *et al*. 1998)) for the observation of optically induced lasing. An elegant way of circumventing this problem has been proposed by the group of Dodabalapur and co-workers (Berggren *et al*. 1997), which exploits blends of different conjugated materials in order to allow transfer of the excited states from the material where the excitation is generated to the one where it can eventually decay radiatively. This 'cascade' scheme, which relies on Förster transfer, increases the flexibility in the design of the structures for both optical and electrical injection, since it provides a greater freedom in the choice of the materials according to their optical or electrical properties. For example, hole or electron transport molecules can be used as hosts. To the best of our knowledge, however, electrically injected lasing has not yet been observed, with this or other schemes. In this respect we consider that, although injection polymer lasers may be technically attainable in the near future, it is hard to forecast such devices as real products for several years, even in the most optimistic predictions. This is because injection lasing is likely to require currents of the order of kA cm^{-2} or higher. Although achievable (Tessler *et al*. 1998), these are too high for long-term operation without significant degradation. In addition, solid state inorganic lasers are well developed and offer a strong competition. Still, we regard the quest for the injection laser a fertile stimulus to the investigation of organic semiconductors, which has led already to a better understanding of the materials and to the design of better LEDs.

In fact, the class of organic semiconductors still offers plenty of opportunities for enlarging the knowledge of the 'soft state' properties. For example, the scheme presented in figure 4 is highly simplified, and does not make any attempt to describe disorder-induced effects, which are very important.

The presence of morphological disorder profoundly affects the electronic structure, originating a distribution of allowed states that influences optical and charge transport processes. In addition to the inhomogeneous broadening of the spectral linewidth, an optical signature of this electronic disorder is the so-called 'spectral diffusion' of the excitons, before radiative decay. When the excitons are photogenerated with energies well above the absorption edge, they migrate from shorter conjugated segments of the polymer chain to longer conjugated segments. This process stops when the excitons find the chain segments with the lowest energy among those accessible through the relevant energy-transfer mechanism (essentially Förster transfer), and is clearly evident in the slight red-shift of the emission spectra in the first 300 fs after photoexcitation.

A similar influence on the transport of charged excitations under the action of an electric field is expected to be exerted by the presence of a (Gaussian) distribution of energies for the charged particles, and models have been put forward in order to account for the experimental results (Roth *et al*. 1989; Schein 1992; Bässler 1984). We observe, however, that a microscopic description of electric transport that is fully consistent with experiments has proved to be very elusive, possibly because of the combination of the effects of disorder, differences among the materials, and of the limited understanding of the interchain effects in the solid state. In this context, the ability to measure the single chain hole and electron mobility, as reported by Hoofmann *et al*. (1998) has been a significant step forward. By means of a time-resolved microwave conductivity technique and pulsed ionization (3 MeV electrons) of single chains of poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, dispersed in benzene, they determined intrachain mobilities in the range of 0.5 and $0.2\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$ for electrons and holes, respectively. The results are very interesting for at least two reasons. First, they show that, at variance with the traditional view of transport in organic semiconductors, electrons may be more mobile than holes, once extrinsic factors are removed. Second, they prove that there is a good prospect for the development of polymer based electronics requiring fast switching times and high carrier mobilities. Incidentally, comparable values of the mobility have been inferred from high-voltage pulsed electroluminescence (EL) experiments in PPV-based LEDs (Tessler *et al*. 1998). An interesting issue at this point is whether there is scope for further improvements of the solid state mobilities, i.e. if interchain mobility via hopping processes can be higher than the intrachain one, and if both intra- and interchain mobilities can be raised further via appropriate material design and preparation, for example by control and enhancement of the intermolecular interactions, of the chemical structure and microstructure, or of the purity. Substantial progress has been reported lately in polymer field-effect mobilities (Dodabalapur *et al*. 1998; Sirringhaus *et al*. 1998), via improvement of order and control over extrinsic doping, indicating that not only are these important factors, but that it is indeed possible to control them.

Issues such as the control of the chemical microstructure (*cis*/*trans* content and molecular weight of the macromolecules (Feast *et al*. 1999), or degree of crystallinity (Barta *et al*. 1998)) and the influence on PL or transport are starting to be addressed, and we consider that the next generation of materials should take advantage of more refined chemical synthesis, in addition to considerable information gathered with first generation materials. Control of the supramolecular film structure via self-organization phenomena is particularly attractive here, in view of the versatility with which organic chemistry can functionalize the materials, and of the advanced understanding of certain self-organizing processes in the biosciences. Several areas can act as fertile grounds or catalysing agents for the development of supramolecular devices and we would like to mention here that the nature of the excited states in conjugated polymers makes these good candidates for nonlinear optical (NLO) phenomena (two and three photon absorption, and second and third harmonic generation). The vast area of sensors, biosensors, and actuators is another example, since the chemistry of some organic semiconductors is very similar to that of some biomolecules (see for example figure 2: the all-*trans* retinal, a conjugated oligomer associated with visual processes), and it is then possible to attempt the use of conjugated polymers for transduction of biological information.

2. Real world applications of conjugated materials: the technological challenge

The possibility of turning interesting properties into useful devices is very important and goes beyond the relevance of the application as such. In the first place it creates the motivation for substantial research spending. Secondly, some devices are in fact specialized scientific tools in their own right, allowing sophisticated measurements of certain material properties. This is the case, for example, of the charge mobility in field-effect transistors (FETs), of the luminescence efficiency and time decays in LEDs, and of charge generation via exciton splitting processes in PV cells. We consider in what follows a number of applications, which represent what we could call ‘first generation’ devices, such as LEDs, FETs, and PV cells. Among these we will focus on LEDs, which after the use of organic photoreceptors for xerography, are the next application of organic semiconductors with the potential of becoming commercially significant on a large scale.

(*a*) *Light-emitting diodes*

A schematic of a typical LED is shown in figure 5*a*. The structure consists of one or more thin films of an electroluminescent polymer sandwiched between two electrodes. At least one of the electrodes has to be transparent in order to ensure efficient light output, and indium–tin oxide (ITO) has become a conventional choice, although it is not the ideal material for a variety of reasons discussed below.

One of the main advantages of polymer semiconductors is that they can be prepared via solution-processing techniques, such as spin-coating or blade-casting, and, more recently, ink-jet printing (Hebner *et al*. 1998). Processability in solution requires grafting of solubilizing side-chains to the polymer backbone, or use of a non-conjugated soluble precursor, as for PPV. This precursor can be deposited from solution onto the suitable substrates and then converted to the conjugated polymer by solid state pyrolysis under vacuum. The thermal ‘conversion’ also releases HCl, which interacts with ITO and generates species responsible for substantial luminescence quenching. It would be highly desirable, therefore, to be able to replace ITO with a less reactive anode, but no material at present can offer a better alternative in terms of transparency, low resistivity, ease of processing and low cost. Among other features, the

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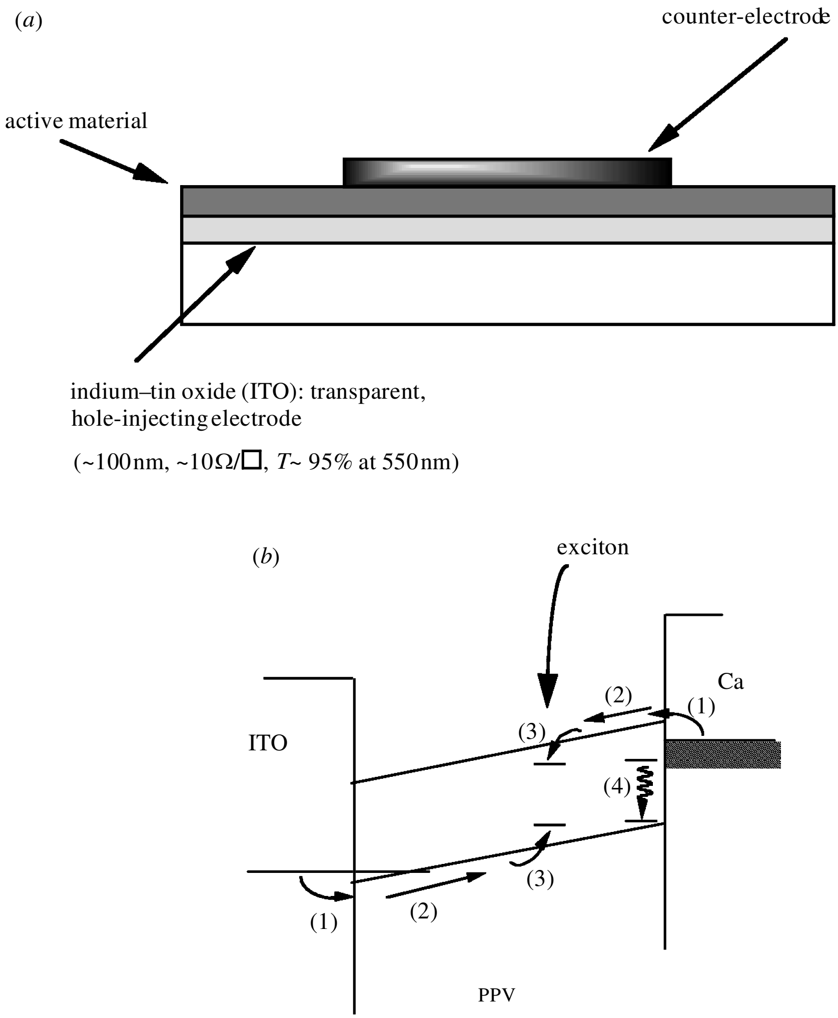

Figure 5. (*a*) Schematic structure of an organic LED. (*b*) The four main processes involved in electroluminescence (EL), i.e. carrier injection (1), carrier transport (2), exciton formation via mutual capture of carriers with opposite sign (3), and exciton radiative decay (4).

ITO electronic properties (work function, carrier concentration and mobility) are also very sensitive to the nature of the surface, and we have shown recently that an oxygen-plasma treatment is effective at increasing work function, hardness, smoothness, and carrier concentration, and therefore at improving efficiency, luminance and lifetime of the LEDs (Kim *et al.* 1998). Interestingly, the lifetime is also improved when a doped hole transport layer (HTL), such as poly(3,4-ethylene dioxythiophene), PEDOT, is incorporated between the ITO anode and the emissive layer (Kim *et al.* 1999).

The top layer is usually the negative electrode, or cathode, since the ITO work function matches more closely the highest occupied molecular orbitals (HOMO), i.e. the 'molecular' equivalent of the valence band, than the lowest unoccupied molecular orbital (LUMO), i.e. the 'molecular' equivalent of the conduction band. In fact, the electron affinity (EA) of most organic semiconductors is between 2.5 and 3 eV below vacuum, whereas the ionization potential (IP) is close to 5 eV below vacuum. Therefore, in order to reduce the energy barrier for carrier injection, low work function materials are better suited as electron-injectors (cathodes), whereas high work function materials, such as ITO (work function *ca.* 4.4–5 eV), are more efficient as hole-injecting contacts (anodes).

The electroluminescence process, i.e. the light emission from these structures under the action of an electric field, can be divided into at least four sub-processes, namely, charge injection (1) and transport (2), opposite charges' recombination and exciton formation (3), and radiative recombination of a fraction of the formed excitons (4) (figure 5*b*). Upon application of an electric field, charge carriers of opposite sign are injected from the electrodes and transported across the polymer. Once injected, each carrier can interact with an oppositely charged particle, and form a coulombically bound exciton, or can be swept across the whole polymer film and finally be ejected into the other electrode.

Much of the LEDs technological challenge revolves around the improvement of the emission efficiency, which is affected by several factors that we now consider in some more detail.

For an LED with non-phosphorescent active materials the EL efficiency can be expressed as (Greenham & Friend 1995):

$$\eta_{\mathrm{EL}} = \eta_{\mathrm{PL}} r_{\mathrm{st}} \gamma_{\mathrm{cap}}, \tag{2.1}$$

where η_{EL} is the EL efficiency, η_{PL} the PL efficiency, r_{st} the number of singlets over the total number of excitons formed, and γ_{cap} the number of excitons formed per unitary charge flowing in the circuit. From equation (2.1) we appreciate the importance of both having a high PL efficiency, and also a balanced injection of carriers. The fate of the formed excitons will depend on the available decay channels, mainly non-radiative for triplets and radiative and non-radiative for singlets. In zeroth order approximations it has often been assumed that the capture efficiency for formation of singlets and triplets is the same, and hence that the upper limit to the electroluminescence efficiency η_{EL} is $\eta_{\mathrm{PL}}/4$ (since the number of triplets will be three times as high as the number of singlets for a random spin distribution of the injected carriers). Recent theoretical studies, however, have indicated that the formation probability of singlets can be significantly different from that of triplets, and hence that the electroluminescence efficiency can be higher than $\eta_{\mathrm{PL}}/4$ (Shuai *et al.* 2000).

The situation changes substantially if phosphorescence (i.e. radiative decay of the triplets) is partly allowed, since in this case a term for the triplets must be added to the expression in equation (2.1). Indeed, it has been demonstrated that highly phosphorescent molecules can be exploited (Baldo *et al.* 1998; Cleave *et al.* 1999) and that the internal EL quantum efficiency can reach up to 90% of the total PL efficiency. Also, in order to avoid concentration quenching of the luminescence, the phosphorescent molecules (such as porphyrins) should be dispersed within other molecular or macromolecular hosts. Transfer of the excitations from the host to the guest then happens via a combination of both Förster (long-range dipole–dipole mechanism) and Dexter (short-range) transfer. Although the total efficiency is lower than the best values obtained with non-phosphorescent semiconductors, research in this direction has just begun, and better results should be possible.

The relationship between cathode work function and efficiency has been the focus of early investigations (Braun & Heeger 1991), and it has been clearly shown for Ca, Mg, and Al that an increase of the work function leads to a decrease in the efficiency. This is often taken as an indication of the presence of an energy barrier at the cathode interface, although it should be emphasized that the nature of the interfaces is complex, owing to the interaction of the metals with the polymer and the oxygen contaminations. The reactivity of Ca and Al with conjugated polymers and oligomers has been studied in detail by Salaneck *et al*. (1996), who used photoelectron spectroscopy in order to study the modifications of the electronic structure of the conjugated materials during the early stage of the metal evaporation in ultra-high-vacuum (UHV). Al is found to disrupt the conjugation of polymers such as PPV by forming covalent bonds, whereas Ca dopes the semiconductors by charge transfer. In addition, Ca is found to diffuse rapidly into the polymer and to lead to short-circuit formation, if evaporated in a UHV environment (*ca.* 10^{-10} mbar), but this problem can be eliminated by evaporating in a less clean environment (*ca.* 10^{-7} mbar), so as to allow the Ca to be partly oxidized and to form an oxide layer, which seems to act as a diffusion barrier. A thin oxide layer has also been found in other studies (Gao *et al*. 1992), and is likely to play a significant role in the limitation of the hole-current and hence in the efficiency increase. Interestingly, a thin layer of lithium fluoride between the emissive polymer and the cathode has been reported recently to reduce Al cathodes work function (2.5 eV) and also to improve efficiency and maximum luminance of the LEDs (Matsumura & Jinde 1998).

Although underestimated initially, injection processes at the anode are also very important, as has been shown by the very substantial improvement obtained by inserting a polymeric or oligomeric HTL between the EL polymer and the ITO. These HTLs can be poly(styrene sulphonate), PSS-, doped PEDOT (Carter *et al*. 1997), polyaniline doped with camphor-sulphonic acid (Karg *et al*. 1996), or other materials with a high IP, which help to reduce the energy barrier for hole-injection and also, by increasing the distance between the radiating dipoles and the electrode, reduce the quenching due to physical and chemical interactions between the two.

Since holes are more mobile than electrons and recombination happens closer to the cathode than to the anode (Lemmer *et al*. 1996), other limitations on the efficiency come from physical interactions of the excited molecules with the metal, and of these the most important are excitation of plasmons in the cathode and the reduced intensity of the electromagnetic field close to a mirror, which, in a first approximation, imposes a node of the field on its surface (Drexhage 1974). PLEDs are complex optical structures with significant reflection and refraction taking place at interfaces (Burns *et al*. 1996), and it is therefore important to control the position of the recombination region in order to maximize constructive interference.

A possible strategy for the control of the efficiency is the use of several polymer layers in the same LED structure. This is an old strategy in the field of organic electroluminescence and was first reported by Tang *et al*. (1987) and Tang & van Slyke (1989) for LEDs made with low molecular weight materials, and is based on the formation of a barrier for one or both types of carriers at the heterojunction, due to the difference in the HOMO and/or LUMO levels. The main issues that can be addressed in this way are as follows:

(i) limitation of the excess majority carrier;

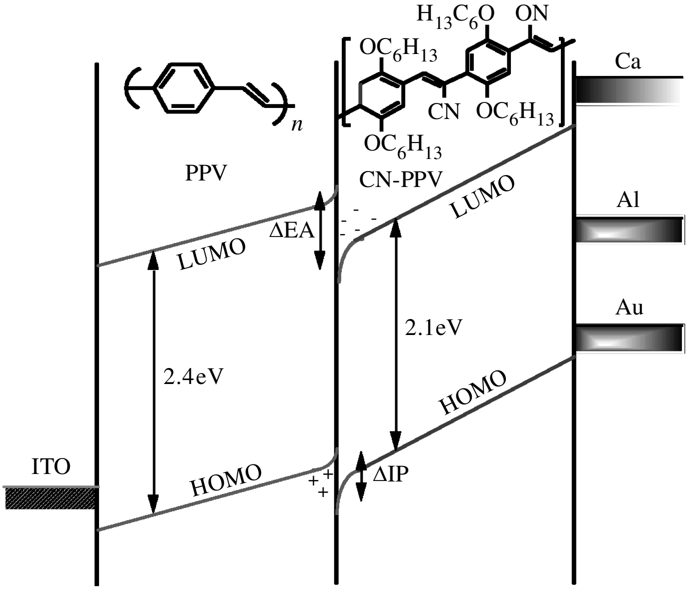

Figure 6. Band diagram of a PPV/CN–PPV heterojunction (see figure for the chemical structures). Note the band offsets at the heterojunction.

(ii) control of the position of the recombination region within the device;

(iii) minimization of the offsets between the electrode work function and the HOMO or LUMO of the polymers.

In the case of polymers significant examples are represented by the PPV/CN–PPV heterojunction (figure 6; Greenham *et al.* 1993), and three-layer structures using an intermediate PVK layer in order to limit the hole excess (Cacialli *et al.* 1996).

The major drawback of the heterojunction approach is the increase in the driving field required for a fixed luminosity, due to the mentioned charge transport barriers. This causes a higher power dissipation, and ultimately an accelerated device degradation. In this respect the use of blends of different organic semiconductors is much more promising, since it allows a larger interfacial area between different polymers without necessarily introducing energy barriers. Recently, we also observed that suitable blends can increase the ratio between the EL and the PL quantum efficiencies, which is likely to arise from an improved capture cross-section, and hence higher probability for formation of excitons γ_{cap} (Cacialli *et al.* 1998).

Another interesting way of controlling the luminescence is via incorporation of the LED into a microcavity structure (Dodabalapur *et al.* 1994), i.e. an optical resonator where the mirrors are spaced at a distance comparable with the wavelength of visible radiation. In particular, OLEDs lend themselves for fabrication into planar Fabry–Perot resonators. In figure 7 we see that substantial narrowing of the spectrum (down to 4 nm) and enhancement of the emission in the forward direction (more than an order of magnitude) can be achieved with these structures (Grüner *et al.* 1996). The confinement of the photon density of states achievable with planar cavities is too limited, however, to allow substantial improvement of the overall emission efficiency (Hayes *et al.* 1997), justifying the significant effort now being directed to

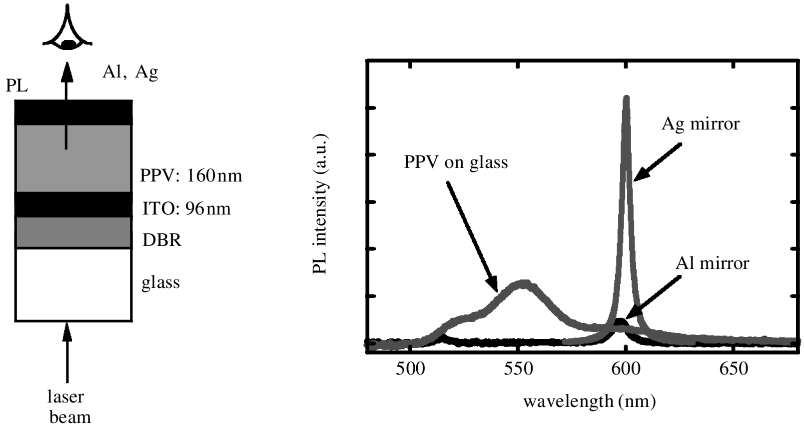

Figure 7. Planar microcavity structure (left) and the optically excited emission spectra in the forward direction, compared with a non-cavity structure. Note also the substantial difference in intensity when using Al or Ag as the top mirror.

the study of structures with photon confinement properties that are extended in two or three dimensions, such as photonic crystals. These are structures for which the periodic alternation of different refractive index materials can produce 'allowed' and 'forbidden' bands for the propagation of the electromagnetic fields, in the same way a periodic potential in crystalline semiconductors produces allowed and forbidden bands for electron propagation. Note, however, that all the photonic structures (planar cavities and photonic crystals) are more expensive than the standard OLEDs, which do not rely on photon confinement effects, and are, hence, commercially less attractive.

As can be appreciated from these brief notes, the technology is still under development and not yet mature. Although the polymer 'bulk' should withstand the application requirements in terms of high PL efficiency and low photobleaching yield (related to the material stability (Staring 1997)), much is still to be learnt about the optimization of both the electrode–semiconductor interfaces and the polymer microstructure. An increasingly important issue here, especially in view of the growing use of random or block copolymers and of polymer–polymer or polymer–oligomer blends, is the occurrence and the control of phase separation phenomena.

Nonetheless, the level of the technology is already well advanced in absolute terms. LEDs with luminous efficiency up to 22 lm W^{-1} at 100 cd m^{-2} and 2.6 V in the green, and 3 lm W^{-1} at 100 cd m^{-2} and 3.8 V in the blue, have been demonstrated by Cambridge Display Technology (CDT). Many firms have by now entered the competition for a share of the markets, and shown prototypes with lifetimes in the range of 10 000 h. Pioneer and Philips in particular are working hard to reach the beginning of the next millennium ready for large-scale production, and many, including Seiko–Epson and CDT, are focusing on more ambitious graphic displays, such as that in figure 8.

(b) *Field-effect transistors*

Organic FETs, like their inorganic counterparts, are essentially a voltage controlled switch and therefore can constitute the elementary logic unit of more complex digital

Figure 8. EL polymer graphic display prototype (courtesy of Cambridge Display Technology Ltd and of *Physics World* June 1999, p. 35.).

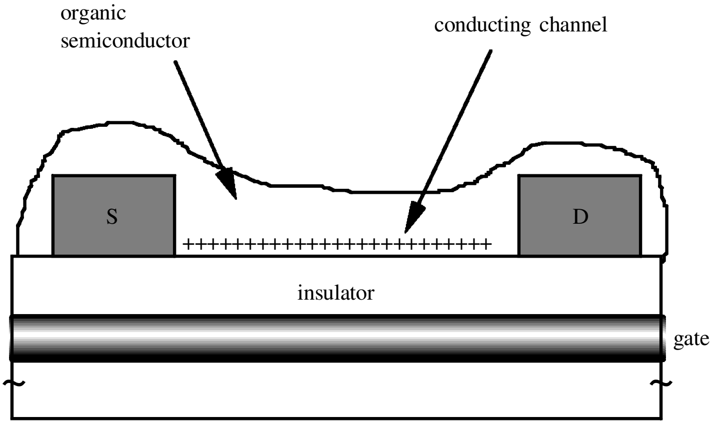

Figure 9. Schematic structure of an organic FET (S, source; D, drain).

circuits. As such, they attract interest for all those applications requiring cheap and disposable, large-area or lightweight logics. A typical application is, for example, the replacement of bar codes with 'smart cards', which can radio-communicate with an electronic reader; these are superior to bar codes since they do not require 'line of sight' visibility by the reading head.

The structure of an organic FET is shown in figure 9. The control electrode or gate is separated from the semiconductor by an insulating layer, on top of which the source

(S) and drain (D) contacts are patterned. The semiconductor is then deposited on top of the whole structure via evaporation (oligomers) or solution processing techniques (polymers). When the gate voltage exceeds a threshold value (V_0), charge carriers are accumulated (or depleted) in the region at the interface between the insulator and the semiconductor, and form (or remove) a 'channel', which allows the current to flow between source and drain. This current saturates when the voltage between the two electrodes exceeds a value that determines the 'pinch-off' of the channel in the proximity of the drain and, under this condition, the source–drain current can be expressed as in equation (2.2). Here W is the width of the electrodes, C_i is the insulator capacitance per unit area, L is the channel length, μ the (average) carrier mobility, and V_g the gate voltage):

$$I_\mathrm{D} = \frac{WC_\mathrm{i}}{2L}\mu(V_\mathrm{g} - V_0). \tag{2.2}$$

Important parameters for the operation of an FET are (a) a high carrier mobility μ, in order to ensure fast switching between the ON/OFF conditions and the required current at low bias, and (b) a high ratio of the currents between the ON and OFF states (ON/OFF ratio), in order to reduce power consumption in the OFF condition.

Although early studies of FETs used polymers such as polythiophene (Tsumura *et al.* 1986), most research until recently has focused on sublimed oligomer films, as the better order of the latter could reproducibly yield better performance, with mobilities in the range of 0.01 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (Dodabalapur *et al.* 1995). Recently, however, a better control of (a) the solid state ordering via manipulation of the regio-regularity, (b) the film-forming properties via optimization of the solvent, and (c) the post-deposition treatments, has allowed substantial improvements also for polymers (Dodabalapur *et al.* 1998; Sirringhaus *et al.* 1998; Bao *et al.* 1996), with mobility reaching 0.01 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and an ON/OFF ratio of up to 10^8. In particular, this allows driving of organic LEDs in 'smart pixels', which would be required by active matrix displays. The possibility of using solution processing instead of vacuum sublimation is obviously much more attractive because of the lower production cost. By exploiting the ability to make both n and p channel FETs, simple circuits such as ring-counters (Brown *et al.* 1995) and other 'all organic' logics have also been demonstrated (Drury *et al.* 1998), proving that all 'plastic' electronics can find a position in the market.

(*c*) *Photovoltaic cells*

Another area of applications of organics is in the fabrication of solar cells and photodetectors. For these, conjugated molecules can again take advantage of cheap and easy fabrication over large areas, and also of relatively high absorption coefficients, deriving from high oscillator strengths for the optical transitions (absorption coefficient $\alpha \approx 10^5\ \mathrm{cm^{-1}}$). The structure of the devices and the fundamental processes are essentially the same as for LEDs, although the aim is now different. The fundamental processes are, in sequential order:

(i) exciton generation via photon absorption;

(ii) exciton splitting;

(iii) charge transport through the active layer;

(iv) charge collection at the electrodes.

In order to maximize the efficiency and the electrical power generation, the absorption coefficient should be as high as possible over a large spectrum. Exciton ionization is particularly efficient at the electrodes' interfaces or at organic–organic heterojunctions between materials with large differences in the EA and IP. Doping with good electron acceptors, such as C60, leads to good efficiency, because of the high EA. In the case of polymers good results can be obtained with blends of CN–PPV and MEH–PPV, which are sufficiently different to phase separate, and provide a large interface area, in addition to a good exciton splitting efficiency due to the different EA (*ca.* 3.4 eV for CN–PPV versus 2.9 eV for MEH–PPV (Halls *et al.* 1995)). Charge collection is not optimum in such blends, however, and better efficiencies (29% quantum efficiency at optimum wavelength, 1.9% overall power conversion efficiency under a simulated solar spectrum), can be obtained by a lamination technique (Granström *et al.* 1998), which still allows the formation of a diffuse heterojunction while permitting a greater control over which polymer is in contact with the anode or the cathode. Another extremely promising variant for this class of devices is that using dye-sensitized mesoporous films of TiO_2 for which replacement of the liquid electrolyte with a solid charge-transport material in an extremely efficient cell (33% quantum efficiency) has been demonstrated lately (Bach *et al.* 1998).

Regarding the prospects for commercialization, these are less advanced, and therefore more challenging than for LEDs. The problem of durability is here more serious than for LEDs, because the latter do not have to withstand intense solar irradiation as a condition of their operation. In our opinion it is likely that further progress on organic PV cells will be fostered by the OLEDs' development, although it is hard to predict now if and when organic PV cells will become cheaper and more widespread than inorganic ones.

The durability problem may be less severe for application of these devices as photodetectors. A possible area of interest that has not been explored so far is, for example, that of astronomical observations, where the flexibility of the cells could be an added bonus in the fabrication of 'adaptive' optics, i.e. cells which can be deformed in order to correct for atmospheric fading or mirage effects.

3. Conjugated molecules and beyond: what next?

An interesting prospect for development of the field is related to the chemical analogy of conjugated molecules with those of biological origin, which virtually opens the way to biocompatible structures and devices, and maybe to artificial organs with complex functions, such as retinas. Before adventuring into futuristic considerations we should note, however, that there is already a huge literature regarding the study of sensors and actuators that use conjugated polymers as the transducers of chemical and biological information into electrical signals or vice versa of the electrical stimulus into movement (actuators) (Smela *et al.* 1995). This is a very broad area that we cannot touch upon, except for a cursory mention to artificial noses based on conjugated polymers, which are particularly well developed, with 200 commercial instruments already delivered by AromaScan (http://www.aromascan.com), a spin-off company of the University of Manchester.

In the last 20 years the biological sciences have witnessed very substantial progress in the understanding of the chemistry of living organisms. As in the best sciencefiction novel, tools have been gathered that allow the manipulation of the several expressions of life in animals and in vegetables.

However improbable though it may seem today, we consider it likely that conjugated molecules will be studied in conjunction with biomolecules, not only for so-called 'bioelectronics' applications, i.e. those involving the use of biomaterials in optoelectronic or photonic devices, or mimicking the natural self-organization mechanisms in artificial materials, but also with the aim of replacing parts of the human body. Although at present little is known about the biocompatibility of electroluminescent and other conjugated polymers, this knowledge is likely to grow in the future, as more and more researchers are becoming fascinated by the biosciences. Artificial silicon retinas, for example, have already been implanted in humans in preliminary experiments, and have a better chance of being developed earlier than conjugated polymer analogues. In this and other applications, however, we expect that the extreme chemical versatility of the polymers should lead, in the long term, to molecules that are more specific, and hence better suited for their task.

As with any scientific achievement, we hope a good dose of ethics will accompany sound development of the most advanced applications.

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