Electroluminescence in conjugated polymers

R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund & W. R. Salaneck

Research in the use of organic polymers as the active semiconductors in light-emitting diodes has advanced rapidly, and prototype devices now meet realistic specifications for applications. These achievements have provided insight into many aspects of the background science, from design and synthesis of materials, through materials fabrication issues, to the semiconductor physics of these polymers.

Electroluminescence—the generation of light, other than black-body radiation, by electrical excitation—is a phenomenon that has been seen in a wide range of semiconductors, and for organic semiconductors was first reported for anthracene single crystals in the 1960s[1,2]. These early studies established that the process responsible for electroluminescence requires injection of electrons from one electrode and holes from the other, the capture of oppositely charged carriers (so-called recombination), and the radiative decay of the excited electron–hole state (exciton) produced by this recombination process.

Development of organic thin-film electroluminescence was spurred on in the 1980s through the work of Tang and Van Slyke[3], who demonstrated efficient electroluminescence in two-layer sublimed molecular film devices. These devices consisted of a hole-transporting layer of an aromatic diamine and an emissive layer of 8-hydroxyquinoline aluminium (Alq_3), the structures of which are shown in Fig. 1. Indium–tin oxide, ITO, is used as the hole-injecting electrode and a magnesium–silver alloy as the electron-injecting electrode. A large number of other molecular materials have been used as the charge-transporting or emissive layer in light-emitting diodes (LEDs). There has been a great deal of activity, particularly in Japan, in the development of devices of this general type; very high levels of performance have been reported, with quantum efficiencies (photons out per charge injected) of several per cent[4].

Since the first report of metallic conductivities in 'doped' polyacetylene in 1977[5], the science of electrically conducting polymers has advanced very rapidly. Applications have taken longer to appear, in spite of some well recognized areas of application for processible conductive materials. More recently, as high-purity polymers have become available, a range of semiconductor devices have been investigated; these include transistors[6–11], photodiodes[12,13] and LEDs[14–18]. The potential for commercialization is perceived to be high for these semiconductor devices because they are seen to compete in application areas where the market can bear the costs of development. In particular, polymer LEDs now show attractive device characteristics, including efficient light generation, and there are several development programmes now set up to establish procedures for manufacture. The principal interest in the use of polymers lies in the scope for low-cost manufacturing, using solution-processing of film-forming polymers.

In parallel with these development activities, much progress has been made in the understanding of the underlying science that controls the properties of these devices. In comparison with inorganic semiconductors, relatively little is known about the electronic properties of these materials; even the nature of the semiconductor excitations remains controversial. There has been considerable progress made recently in resolving some of those issues which determine the limits to device performance. These relate to the intrinsic electronic structure of the polymers (for example, the energetics of triplet excitons, and the engineering of high luminescence efficiency in the presence of strong intermolecular interactions), and also to the scope for 'optical engineering' of the devices—to achieve effective coupling between electronic excitations in the polymer and the generated photons. Here we discuss the current understanding of the science and technology, covering materials synthesis, materials properties and device properties. This review is not intended to be comprehensive, and we have (for example) made no attempt to cover the wide range of work of the development of materials with controlled colour. We refer the reader also to recent reviews[19–22].

Polymer LED structures

Conjugated polymers derive their semiconducting properties by having delocalized π-electron bonding along the polymer chain. The π (bonding) and π^* (antibonding) orbitals form delocalized valence and conduction wavefunctions, which support mobile charge carriers. The structures of some of those polymers used for LED fabrication is shown in Fig. 2. Electroluminescence from conjugated polymers was first reported in 1990 (ref. 14), using poly(*p*-phenylene vinylene), PPV, as the single semiconductor layer between metallic electrodes, as is illustrated in Fig. 3a. In this structure, the ITO layer functions as a transparent electrode, and allows the light generated within the diode to leave the device. The top electrode is conveniently formed by thermal evaporation of a metal. LED operation is achieved when the diode is biassed sufficiently to achieve injection of positive and negative charge

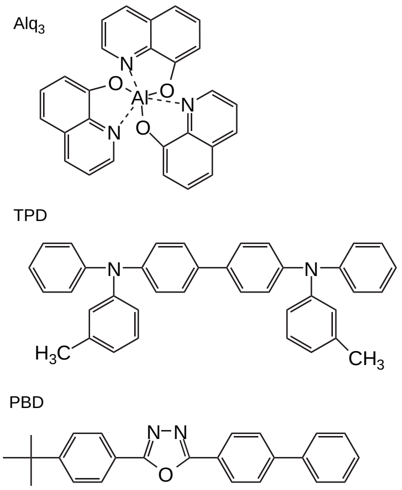

Figure 1 Structures of some molecular semiconductors that have been used in thin-film electroluminescent devices. Alq_3 is used as an electron transport and emissive layer, TPD is used as a hole transport layer, and PBD is used as an electron transport layer.

carriers from opposite electrodes. Capture of oppositely charged carriers within the region of the polymer layer can then result in photon emission.

Diodes of this type can be readily fabricated by solution-processing the semiconducting polymer onto the ITO-coated glass, even though the film thickness is no more than typically 100 nm. Spin-coating from solution has been demonstrated to be capable of producing highly uniform layer thickness, with a thickness variation of no more than a few ångströms spread over several cm^2. Electrodes are chosen to facilitate charge injection; ITO has a relatively high work function and is therefore suitable for use as a hole-injecting electrode; low-work-function metals such as Al, Mg or Ca are suitable for injection of electrons. The band scheme under forward bias is shown schematically in Fig. 3b.

PPV has an energy gap between π and π^* states of about 2.5 eV, and produces yellow-green luminescence in a band below this energy, with the same spectrum as that produced by photoexcitation (Fig. 4)[23]. We note that it shows broadening due to vibronic coupling, as is characteristic for optical transitions in molecular semiconductors where the excited state is confined to the molecular unit, and is described as an exciton.

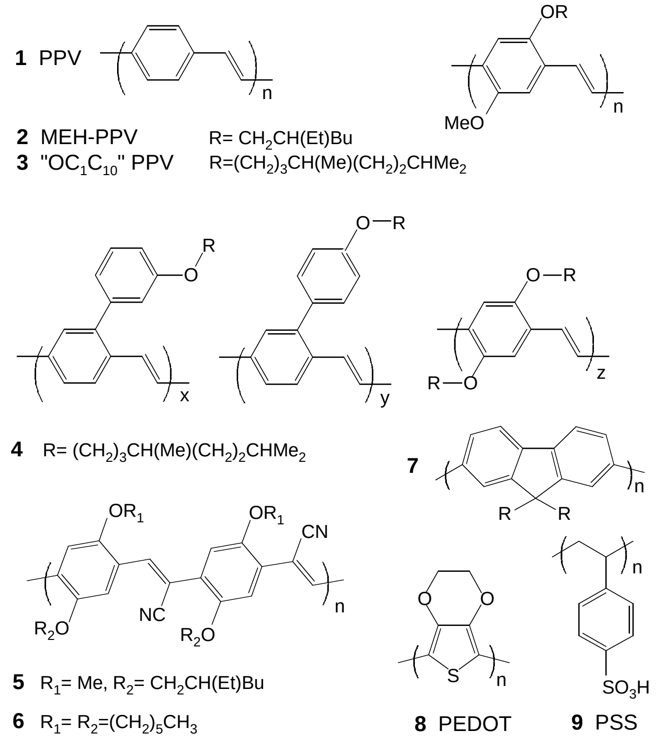

Figure 2 Polymers used in electroluminescent diodes. The prototypical (green) fluorescent polymer is poly(*p*-phenylene vinylene), as shown by **1**. This compound is formed most usually by thermal elimination of tetrahydrothiophene and hydrogen chloride (or bromide for lower temperatures) from a methanol- and water-processible sulphonium precursor[91] prepared by a Wessling condensation polymerization of a bis-sulphonium salt. Condensation polymerization of the bis(halomethyl) monomers affords the two best known (orange-red) solution-processible conjugated polymers MEH-PPV (**2**) and "OC$_1$C$_{10}$" PPV (**3**) which have been much used[20,24]. Copolymers have been widely developed because they allow colour tuning and can show improved luminescence[15]; copolymer **4** has recently been reported to show very high electroluminescence efficiency[25]. Cyano-derivatives of PPV **5** and **6** show increased electron affinities and are used as electron transport materials[16,56]. Many elegant organometallic coupling procedures have been employed to make poly(phenylene)s and related polymers[92–96]. The development of Suzuki condensation coupling, using bis-boronates, has provided an important route to high-purity polymers, including poly(dialkylfluorene)s **7** (ref. 97), which show high luminescence efficiencies[26]. 'Doped' polymers such as poly(dioxyethylene thienylene), PEDOT (**8**), doped with polystyrenesulphonic acid, PSS (**9**), are widely used as hole-injection layers.

The levels of efficiency of the first, simple LEDs based on PPV, which were fabricated with aluminium negative electrodes, were relatively low, of the order of 10^{-4} photons generated within the device per electron injected[14] (an internal quantum efficiency of 0.01%). These values have risen rapidly over the past 5 years as improved understanding of the operation of these devices, aided in considerable measure by parallel developments made with sublimed molecular film devices[3], has allowed considerable optimization of the device characteristics. The use of negative electrodes with lower work functions was shown to improve efficiency[17], and for single-layer diodes of the type shown in Fig. 3, an external efficiency of about 2 lumens per watt (2 lm W^{-1}) has been reported in devices made with ITO/MEH-PPV/Ca (ref. 24). Other early approaches used to increase efficiency include the use of copolymers based on PPV with higher luminescence efficiencies[15], and the use of heterostructure devices[16]. More recently, very much higher efficiencies have been reported for diodes made with similar structures to that shown in Fig. 3, but with a layer of poly(dioxyethylene thienylene) doped with polystyrene sulphonic acid (Fig. 2) between the ITO and the emissive polymer layers. Efficiencies in the green part of the spectrum of up to 16 lm W^{-1} are reported for diodes using copolymer **4** (Fig. 2) with composition $x = y = 47\%$, $z = 2\%$ (ref. 25), and up to 22 lm W^{-1} for emissive polymers based on polyfluorene, **7** (Fig. 2)[26]. Current-density/voltage/luminance characteristics for these polyfluorene-based devices are shown in Fig. 5.

Device operation

A schematic energy-level diagram for a PPV LED under forward bias is shown in Fig. 3b. As described above, polymer LEDs operate by the injection of electrons and holes from negative and positive electrodes, respectively. Electrons and holes capture one another within the polymer film, and form neutral bound excited states (termed excitons). Excitons in conjugated polymers are generally considered to be more strongly localized than excitons in three-dimensional semiconductors, not least because the exciton is substantially confined to a single polymer chain. The spin wavefunction of the exciton, formed from the two spin-$\frac{1}{2}$ electronic charges, can be either singlet ($S = 0$) or triplet ($S = 1$), and a consequence of the confinement of the excitation is that the energy difference between singlet and triplet (the exchange energy) may also be large. Spin-allowed radiative emission (fluorescence) is from the singlet only, and when the exchange energy is large, cross-over from triplet to singlet is unlikely, so that triplet excitons do not produce light emission, other than by indirect processes such as triplet–triplet annihilation, or by phosphorescence.

The internal quantum efficiency η_{int}, defined as the ratio of the number of photons produced within the device to the number of electrons flowing in the external circuit, is given by:

$$\eta_{\mathrm{int}} = \gamma r_{\mathrm{st}} q \qquad (1)$$

where γ is the ratio of the number of exciton formation events within the device to the number of electrons flowing in the external circuit, r_{st} is the fraction of excitons which are formed as singlets, and q is the efficiency of radiative decay of these singlet excitons. As we discuss below, the efficiency of radiative decay depends on the device structure, being strongly affected by the photonic structure of the device (for example, the proximity of metallic mirrors).

In order to achieve efficient luminescence, it is therefore necessary to have good balancing of electron and hole currents, efficient capture of electrons and holes within the emissive layer, strong radiative transitions for singlet excitons, and efficient coupling of these excitons to photon states allowed in the device structure. We now discuss these topics.

Electrode interfaces. Injection of charge from most electrode materials requires that charges surmount or tunnel through a barrier at the interface. This is expected on examination of the positions of the electrode metal work functions and the positions of the highest occupied molecular orbitals (HOMO; π orbitals) and the lowest unoccupied molecular orbitals (LUMO; π^* orbitals) in the polymer. For the case of PPV, ITO provides a relatively good match for hole injection, though there is a barrier of around 0.2 eV (ref. 27). However, electron injection is more difficult to achieve without the use of low-work-function, reactive metals such as calcium (for which the barrier, as determined by the difference in work function of the metal and electron affinity of the polymer, is of a similar magnitude).

The nature of interfaces, between the active light-emitting polymer medium and the metal electrode, or between the polymer and the ITO layer, are of paramount importance in determining device performance. The control of these interfaces ultimately may be among the more important determining factors in the eventual success of light-emitting devices[28]. A combined experiment–theory approach to the study of polymer surfaces and interfaces has been applied to a wide variety of π-conjugated polymers and model molecules, as well as to the early stages of metal-on-polymer (and model molecule) interface formation[28–30]. During the course of these studies, certain general trends have emerged. One particular issue, which is often neglected, is that there is always 'chemistry' that occurs at the interface[28]. Even though the metal-on-polymer interface is discussed here, there is a growing body of evidence that additional, equally important, interfacial effects occur at the polymer-on-ITO interface[31].

The chemistry that occurs at the metal-on-polymer interface varies with the nature of the metal involved, the polymer involved, and especially with the cleanliness of both the materials employed and the vacuum system used in the metallization process. As aluminium and calcium are two of the most commonly used electron-injecting metals, we confine our remarks to effects which occur during the early stages of interface formation involving these two metals on the surfaces of the PPVs.

The deposition of aluminium atoms upon essentially oxygen-free polymer surfaces leads to cluster formation, and to the formation of covalent bonds at the vinylene-carbon atoms of PPV (and substituted PPVs)[32]. Although clustering occurs, just as in the case of aluminium atoms on the surfaces of inorganic semiconductors, atomic diffusion takes place into the near-surface region, and covalent bond formation is localized to within a characteristic length scale; this scale is of the order of an electron tunnelling distance, that is 20–30 Å.

In the case of calcium vapour-deposited upon clean surfaces in ultrahigh vacuum (UHV), it was observed clearly, first for a model polyene molecular solid system and subsequently for substituted PPV[33], that calcium atoms diffuse into the near-surface region, donate electrons to the π-system, and form Ca^{2+} ions. The interfacial region between the Ca-metal contact and the polymer has an approximate scale in the range of 20–30 Å (similar to the case of Al atoms). In contrast, when (as a result of exposure of the sample to air) there are large numbers of oxygen-containing species at the surface of, for example, PPV (ref. 34), the reactions are different: first, an interfacial layer of an oxide of calcium is formed when the calcium atoms are deposited in UHV, and then, after the oxygen-containing species have been consumed by these initial calcium atoms, calcium metal is deposited. The scale of this interfacial oxide (insulating) layer also is of the order of 20–30 Å, depending on the details of the surface contamination, chemical impurity of the polymer, and/or the vapour-deposition environment.

Thin barrier layers at the semiconductor/cathode interface can provide improved LED performance, as was shown for molecular film devices, using layers of ionic salts such as LiF evaporated to thicknesses of the order of 1 nm or less[35]. Such layers probably also occur when cathodes are formed in the presence of a background oxygen pressure. We note that on oxygen-free surfaces of PPV, vapour deposition of calcium in a background pressure of about 10^{-6} mbar of O_2 results in a metallic oxide contact which is observed to increase LED yield, lifetime and luminescence[36]. The calcium-on-PPV results are summarized in Fig. 6, where either a doped conducting polymer layer is formed on the oxygen-free surface of PPV, or a calcium oxide layer is formed on the surface of PPV containing large amounts of oxygen-containing species.

Turning to the anode: ITO has been the usual choice of material. However, although it has the virtue of optical transparency, it is not a well controlled material. There have been several reports of the use

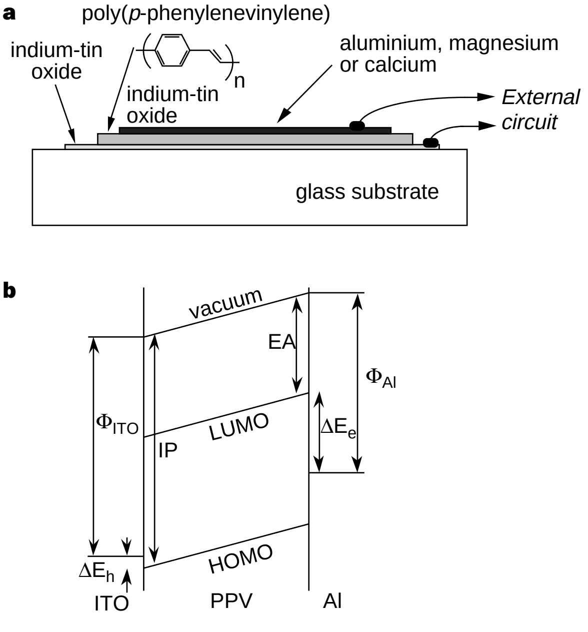

Figure 3 Structure and schematic energy-level diagram of a single-layer polymer electroluminescent diode. **a**, Device structure. **b**, Schematic energy level diagram for an ITO/PPV/Al LED, showing the ionization potential (IP) and electron affinity (EA) of PPV, the work functions of ITO and Al (Φ_{ITO} and Φ_{Al}), and the barriers to injection of electrons and holes (ΔE_e and ΔE_h). There is a small barrier for hole injection from the ITO electrode into the valence band states (or highest occupied molecular orbital, HOMO), and, with aluminium as cathode, a considerably larger barrier for electron injection into the PPV conduction band states (or lowest unoccupied molecular orbital, LUMO).

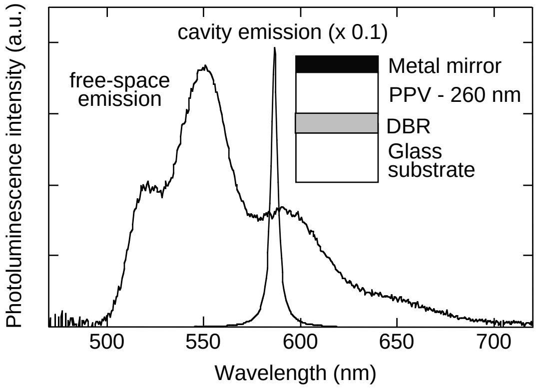

Figure 4 Photoluminescence spectra from PPV. Shown is the optically excited luminescence from PPV as measured for a thin film on a glass substrate (free-space emission) and from a microcavity structure (dimensions as shown) (a.u., arbitrary units). Similar microcavity devices which can be electrically excited are made by forming a layer of ITO onto the distributed Bragg reflector (DBR) mirror before deposition of the polymer layer[23].

of chemically doped conjugated polymers as injection electrodes. Several p-doped conjugated polymers show good environmental stability, including polypyrrole, polythiophene derivatives (Fig. 2) and polyaniline, and such materials have been used as hole-injecting electrodes[37–39]. Several groups have reported not only improved device efficiency, but also considerably improved device uniformity and longevity[21,24,40,41]. These doped polymer electrodes have high work functions, thereby providing low barriers for hole injection to the semiconductor layer. It is also likely that there is at least some diffusion of the dopant in the 'electrode' layer to the 'semiconductor' polymer layer, to give a dopant profile into this layer. Though this is clearly desirable in order to achieve easy charge injection, such a diffusion process must be restricted close to the interface, to provide stable operation over long times. We note that most reports of stable operation over long operating times are for devices which use polymeric dopants, which are expected to be relatively immobile. These include polystyrenesulphonic acid, **9**, as used to dope the polythiophene derivative, PEDOT, **8**, shown in Fig. 2.

Pei *et al.*[42] have shown that with the addition of a salt and ion-transporting material such as poly(ethylene oxide) to the conjugated polymer, very low barriers for charge injection are found. They attribute this to the formation of p-doped regions in the polymer near the positive electrode and an n-doped region near the negative electrode, with the doping arising from electrochemical reactions which occur under drive conditions. Another very important process is the pile-up of mobile ions at both electrode interfaces under the applied field. The very high ionic charge density at the interfaces that can be produced in this way screens the energy barrier for charge injection over very short distances (less than 1 nm), so that tunnelling through this barrier is easy[43]. The effect of mobile ions on long-term operating stability is not reported, however, although the immobilization of these ions has been discussed[44].

Charge injection and charge transport. In spite of the very clear evidence for strong chemical interactions between polymer and metal, there is clear evidence that the size of the barriers for electron and hole injection still scales with the electrode work functions. This has been shown in measurements of internal electric field[45].

The process of charge injection from metal electrodes and the process of charge transport within the polymer layer are difficult to disentangle on the basis of the device electrical characteristics, and the present literature can be confusing. For diodes with large barriers for charge injection (Fig. 3b), the injection of charge, either by thermionic emission or by tunnelling, can certainly limit current flow[46,47]. However, charge injection is not considered to limit current flow for LEDs which show good operating characteristics, such as the low turn-on voltage shown in Fig. 5. Instead, current flow is bulk-limited, principally through the build-up of space charge[48]. The space-charge-limited current regime is easily achieved in these structures because the low-field mobilities of charge carriers in relatively disordered molecular semiconductors is very low—less than $10^{-6}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ as modelled by Blom *et al.*[48].

Modelling of the process of charge injection, taking into account the nature of the available states in the organic semiconductor, produces injection rates consistent with experiment[49–51]. Modelling of space-charge-limited currents is complicated by the need to take account of a strongly field-dependent mobility[52], and the influence of bipolar currents on the reduction of the bulk space charge[53].

We note that the type of device that produced the characteristics shown in Fig. 5 has both hole-injecting and electron-injecting electrodes with relatively low barriers for charge injection, so that high current densities and concomitant light emission is produced at low voltages. As regards the cathode, calcium is not particularly convenient to handle, but magnesium (alloyed with silver), which is

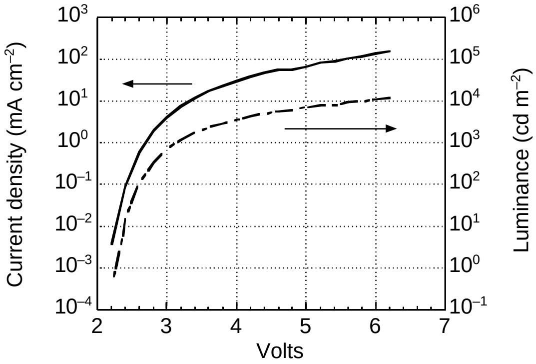

Figure 5 Current density and light output versus drive voltage for green-emitting polymer LEDs based on polyfluorene[26]. These diodes show turn-on for current and light near 2 V applied bias, and reach 100 cd m^{-2} at 2.6 V, and 1,000 cd m^{-2} at 3.1 V. Peak efficiencies of 22 lm W^{-1} are achieved near 100 cd m^{-2}. As discussed in the text, current flow is considered to be bulk-limited, rather than injection-limited for devices such as these with low turn-on voltages.

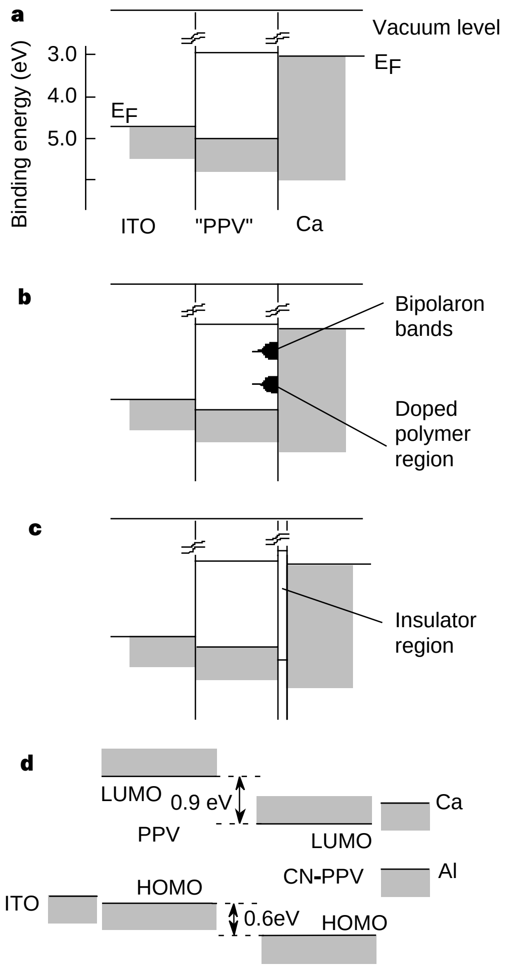

Figure 6 Energy levels for electroluminescent diodes. **a–c**, An ITO-PPV-Ca diode before contact between the three layers, illustrating the energies expected, **a**, from the metal Fermi energies, assuming no chemical interactions at the interface, **b**, after some 'doping' of the interfacial layer of PPV by Ca, setting up 'bipolaron' bands within the PPV semiconductor gap (note that the Fermi energy for the 'doped' PPV lies between the upper bipolaron level and the conduction band), and **c**, after interfacial chemistry which sets up a blocking layer at the interface (as expected in the presence of oxygen). **d**, Energy levels for the components of a two-layer heterojunction diode fabricated with PPV and CN-PPV.

widely used for sublimed molecular film diodes, does not produce such good performance. But aluminium alloyed with low-work-function metals can provide an air-stable material which also gives good performance[41].

Injection and transport of holes from the positive electrode into the bulk of the polymer film must be matched by injection and transport of electrons from the opposite electrode. Recent results from the authors' laboratories obtained with single-layer devices of the type characterized in Fig. 5 indicate that reasonably efficient current balancing can be obtained in these structures. However, for sublimed molecular film devices, the use of two-layer structures to control injection rates of electrons and holes (by introducing barriers for charge transport at the heterojunction between the two semiconductor layers) has been shown to be a very effective means for obtaining current balance[3,54,55]. Devices of this type made with polymers have been fabricated by a number of groups, most successfully using solution-processible poly(cyanoterephthalylidene)s which are derivatives of PPV with nitrile groups attached to the vinylic carbons (Fig. 2). These complement the existing hole-transporting PPVs. The band scheme for a two-layer device of this type is shown in Fig. 6d. At the interface between the two polymers there are sizeable offsets in the energies of the π orbitals (that is, HOMO) for the PPV and the CN-PPV and also between the π^* orbitals (LUMO) of the PPV and CN-PPV layers. Under forward bias, injection of holes from the ITO into the HOMOs of the PPV layer results in transport of holes to the heterojunction, at which they are confined by the potential barrier which must be surmounted if they are to progress into the CN-PPV layer. Similarly, electrons injected from the negative electrode are confined at the heterojunction by the potential step required to get transfer into the PPV LUMOs. Tunnelling across one or other barrier will allow electron–hole capture and electroluminescence. For these polymers, holes tunnel to the CN-PPV and emission is from this layer (typically in the yellow-red part of the spectrum). External quantum efficiencies as high as 2.5% (for light emitted in the forward direction) are measured with CN-PPV **8** (refs 56, 57).

Electron–hole recombination and light emission. The process of electron–hole capture in these devices is crucial to device operation. In order to get efficient capture in these very thin structures (with a polymer layer total thickness of ~100 nm), it is necessary that one or other charge carrier is of very low mobility so that the local charge density is sufficiently high to ensure that the other charge carrier will pass within a collision capture radius of at least one charge. This is certainly enhanced in the heterostructure devices discussed above, where confinement at the heterojunction causes a build up in charge density. Modelling of charge recombination using Langevin theory has been used by several groups[51,53,58].

Assuming that the electron–hole capture process is spin-independent (as implicit in the Langevin model), excitons should be formed with spin wavefunctions in the triplet and singlet configurations in the ratio 3:1. For these polymeric semiconductors, there is firm evidence that the triplet exciton is strongly bound with respect to the singlet, so that we expect to lose 75% of the electron–hole pairs to triplet excitons which do not decay radiatively with high efficiency. Experiments to detect the presence of triplet excitons have been performed using measurements of electroluminescence-detected electron-spin resonance[59] and by measurement of the allowed optical transition between the lowest-lying triplet and a higher-lying triplet at 1.4 eV (ref. 60). This latter work provides an estimate of triplet concentration which is consistent with the 3:1 branching ratio expected within this simple model.

Schemes to make use of the triplet excitons are clearly attractive. One approach is to introduce species that will allow efficient triplet luminescence (phosphorescence). This can be provided by high-atomic-number elements with strong spin–orbit coupling. A platinum-containing porphyrin has been successfully used as a 'dopant' in both a molecular[61] and a polymeric[62] host; both singlet and triplet excitons generated in the host material are collected at the porphyrin, which shows efficient phosphorescence. A potential drawback with this approach is that the triplet emission colour is generally considerably red-shifted with respect to the singlet emission of the host, and although this is desirable for red emission[61,62], may be problematic for emission colours of green and blue.

Understanding of the nature of the neutral excited states in conjugated polymers has been advanced by a wide range of quantum-chemical calculations[30,63,64]; inclusion of both electron–electron and electron–phonon terms turns out to be essential to establish a coherent picture of the photoexcitations[64]. Figure 7 illustrates some of the issues concerned. High emission requires that S_1, the lowest singlet excited state, be strongly coupled (that is, possess a large oscillator strength) with the ground state, S_0. Soos and co-workers[63] have derived the range of parameters related to electron–electron interaction and bond-length alternation in conjugated polymers which ensure that S_1 is of opposite symmetry to S_0; this is the case in poly(*p*-phenylene) and poly(*p*-phenylene vinylene) but not in polyacetylene. The last is therefore not luminescent.

The nature of the S_1 state itself is of importance, and has long been debated. A broad consensus has now emerged: S_1 is viewed as a polaron-exciton of weak to intermediate binding (at most a few tenths of an electron volt)[65,66]. (By 'polaron-exciton', we mean an exciton associated with a local geometry (lattice) relaxation, a feature fully confirmed by the strong vibronic progression seen in optical absorption and, as seen in Fig. 4, emission.)

Radiative emission from the singlet exciton is conveniently measured as photoluminescence (this depends on only the factor q in equation (1)). There has been considerable progress in the search for conjugated polymers which show efficient photoluminescence in the solid state. Measurements obtained using an integrating sphere have been reported[67]. Luminescence efficiency in the solid state tends to be lower than that measured for isolated molecules; this is due both to exciton migration to quenching sites, and to interchain interactions which produce lower-energy excited states which are not strongly radiatively coupled to the ground state[68]. An important source of quenching sites is provided by chemical doping, and many of the first conjugated polymers to become available were sufficiently doped that luminescence yields were very low. However, the PPVs prepared by the precursor routes show photoluminescence efficiencies between 27% (ref. 67) and

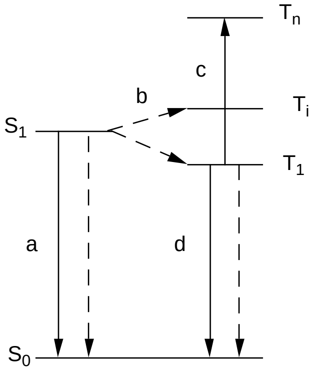

Figure 7 Schematic representation of pathways for singlet decay as well as triplet excitation and decay. Solid arrows represent radiative processes, corresponding to absorption or emission of light; dashed lines denote non-radiative processes. Fluorescence (a), intersystem crossing (b), photoinduced triplet–triplet absorption (c), and phosphorescence (d) are represented. S_0 is the ground (singlet) state; S_1 is the first excited singlet; T_1 the first excited triplet; and T_i and T_n are higher-lying triplet states.

80% (ref. 41), and some of the soluble derivatives, such as the cyano-substituted polymers (Fig. 2) and copolymers, show efficiencies of around 50%.

There is considerable evidence that interchain interactions can significantly modify the energetics of exciton formation in conjugated polymers. For example, interchain interactions are present in the ground state of some of the CN-PPV (ref. 69). The situation for PPV is controversial at present. Measurements at Cambridge of the photoluminescence efficiency (27%) and the decay rate (0.32 ns) are consistent with initial photogeneration of singlet, intrachain excitons which then decay both radiatively (with a lifetime of the order of 1 ns) and non-radiatively[67]. However, Rothberg and co-workers have presented evidence for the formation of interchain charge-separated states[70], though this might be associated with partially oxidized polymer, for which carbonyl groups act as electron traps and facilitate charge separation, as suggested by measurements of photoluminescence excitation spectra[71]. There are several studies of the effects of interchain order and interactions in well-controlled model oligomer systems[72,73].

Photonic structure effects. It is now recognized that the coupling of electronic excitations to photon states is strongly affected by the physical structure of the diode. In device structures of the type discussed here, the presence of the metallic cathode provides a mirror which modifies the pattern of the electromagnetic modes near the cathode, setting up standing-wave states. This has the effect of reducing the radiative emission rates for polymer chains which are placed at the nodal spacings from the cathode, and in addition, there can be energy transfer into plasmon modes in the metal[74]. Studies of model structures, in which a thin semiconducting polymer layer is spaced away from a metallic layer by a dielectric layer (silicon oxide), show the effects of plasmon losses at short distances (<30 nm); strong oscillations due to the standing wave states are also found, with an optimum spacing near 60 nm (dependent on the emission wavelength and the refractive index of the spacer layer)[57]. This is an important consideration for the design of efficient diodes; in this respect, heterojunction devices of the type developed by Tang[3] are particularly convenient, as the recombination process is close to the heterojunction, and this can be placed at the correct position with respect to the cathode electrode by selection of the thickness of the electron-transport layer. For diodes of the type characterized in Fig. 5, where electron–hole recombination takes place over a broader region extending from the cathode, some loss of performance is inevitable. Experimentally, we find an optimum thickness for the polymer layer of around 70 nm.

The polymer LED structure is easily adapted to function as a microcavity device by the addition of a second mirror. This type of structure has been investigated with many materials systems, including sublimed molecular films[75,76] and conjugated polymers[23,77,78]. Both metallic and dielectric (distributed Bragg reflector, DBR) mirrors have been used, as is illustrated by the structure shown in Fig. 4. The Fabry–Pérot etalon formed by the two mirrors defines the allowed cavity electromagnetic modes, which have narrow linewidths for cavities formed with high-reflectivity mirrors. Emission from the excited polymer is only possible into these modes, and only then when the polymer chromophore is placed away from nodes in the standing-wave electromagnetic field pattern. The spectrum shown in Fig. 4 shows the very narrow emission that can be readily achieved. In addition, there is an undesirable angular dispersion of the wavelength (with a blue-shift off-axis), and a considerable redistribution of the angular dependence of the intensity. The latter may be useful when emission is required only in the forward direction; very considerable intensity enhancements in this direction, as seen in Fig. 4 for example, have been reported[23,76]. Such microcavity structures are also capable of supporting optically pumped lasing[79]. We note that considerable efforts are being made to investigate whether it is feasible to construct a polymer injection laser. In spite of the demonstration of high peak current densities (above 1,000 A cm^{-2}), there are considerable intrinsic problems due excited state absorption from injected carriers[80,81].

Efficiency and stability

The model for device operation of polymer LEDs sets some limits to the efficiency of operation. From equation (1), we see that three factors are involved. (1) Charge balancing, covered by γ, is in principle capable of reaching high values, particularly for heterojunction devices. (2) Recombination, covered by r_{st}, is limited to 25% if the creation of excitons is in the ratio 3:1 triplet:singlet. At present, there is only limited information on the energetics of triplet excitons in both polymer and sublimed film devices; though calculations suggest an exchange energy of several tenths of an electron volt for PPV[82], experimental evidence has been hard to find. There may be considerable scope for design of materials with low exchange energies which would show intersystem crossing back to the singlet and therefore more efficient generation of emissive excitons, and as mentioned above, direct use of triplets in phosphorescent emitters[61,62]. (3) Radiative emission from excitons, covered by $r_{st}q$, has now been measured in realistic conditions (the presence of electrodes), and there is rapid progress in obtaining high efficiencies. Values well in excess of 50% are realistic.

The values of efficiency reported for polymer devices, now above 20 lm W^{-1} for green emission (Fig. 5) are now very high, and compare favourably to those reported for sublimed molecular film devices. Among these, devices made with quinacridine-doped Alq$_3$ as the (green) emissive layer[55,83] are reported to show luminous efficiencies of 10 lm W^{-1} at a luminance near 100 candelas per metre^2 (100 cd m^{-2}), and devices with bluer emission show 6 lm W^{-1} (refs 84, 85). On the basis that efficiency is limited to 25% by the singlet–triplet ratio, these numbers are very high, and represent values for the product γq in excess of 50%.

Probably the most critical performance characteristic for organic LEDs is that of device lifetime, both storage and operational. Operating lifetimes in excess of 3,000 hours, and, generally, in excess of 10,000 hours, are required for most applications, and storage times of 5 years or more are required. Important progress has been reported in this area. First, it is clear that all materials, both polymeric and molecular, will photooxidize[86] in the presence of water and/or oxygen (the former is now found to play a very important role[87]). Devices must therefore be encapsulated against ingress of water and oxygen, and though this has been achieved for devices made on glass, there are unsolved problems in achieving adequate performance from flexible substrates[18] (important primarily to allow reel-to-reel coating).

There are many studies of degradation processes now in the literature[21]. Devices under operation often show deterioration through formation of 'black spots', which are commonly attributed to the presence of pinholes in the cathode metal, and to ingress of water/oxygen which can allow delamination of the cathode from the semiconductor[21,88]. It has also been suggested that the oxygen present in ITO may be involved[40].

Limited results on measured lifetime are available in the literature. The best results reported for sublimed molecular films, based on the Kodak structure, give more than 10,000 hours to half initial brightness (300 cd m^{-2}) for devices made with quinacridine-doped Alq$_3$ as the emissive layer, and an Al/Li alloy as cathode[83]. For the polymer devices, there are detailed studies of devices made with "OC$_1$C$_{10}$" PPV reported by the Philips group, under ambient and also accelerated testing conditions[24]. Operation at display-level brightnesses to beyond 10,000 hours is routinely achieved with little loss of brightness under constant current drive. The most problematic ageing process is the gradual rise in drive voltage required to maintain constant current; this can be[24] as much as 70% of the initial drive voltage over a period of 5,000 hours. This is considered to be due to a reduced carrier mobility in the polymer, and has been associated with irreversible chemical changes; whether these are intrinsic or due to extrinsic factors, caused for example by poor encapsulation, is not reported at present.

Towards applications

The performance of organic LEDs meets many of the targets necessary for applications in displays. Backlighting and segmented displays have been identified for early products by Philips, and this company has announced the setting up of a pilot line at Heerlen. Passive matrix-addressed displays are attractive, as the device construction is relatively simple. However, this does require that pixels are driven, row by row, under pulsed conditions, and both resistive losses in the conductive tracks and efficiency reductions for the diodes at high current densities limit the pixel number. Such displays have been developed with the sublimed molecular film devices as alphanumeric displays, (64 × 256; ref. 83), where average luminances of around $100\,\mathrm{cd\,m^{-2}}$ are required (this is a typical computer monitor level), and as far as a 1/4-sized VGA display (320 × 240; refs 84, 85). Extension to a full-colour graphic display (for computer monitors and for video display) is very attractive, not least because organic LEDs provide full viewing angle and video-rate response times (in contrast to current liquid-crystal display technology). However, this required red, green and blue colours with appropriate chromaticity, methods for colour patterning, and also new addressing schemes. Rapid progress is being made with these three problems. Development of full colour has been reported, both for sublimed films[84,85] and for polymers[26]. Solution-processing of polymers offers new methods for colour patterning, among which there is particular interest in ink-jet printing, to place separated pixels of red-, green- and blue-emitting polymers onto the prepared substrate. This is being developed by Seiko-Epson and Cambridge Display Technology[26], and the use of ink-jet printing has also been reported by other groups[89,90]. Active-matrix transistor arrays, modified from those at present used for liquid-crystal displays, can now provide sufficient current-driving capability to meet the requirements of organic LEDs. This is made possible by the improved properties of polycrystalline silicon compared to those of amorphous silicon, and demonstrator active-matrix polymer displays have been made[26]. □

R.H.F. and R.W.G. are at the Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK. A.B.H. is at the Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK. R.H.F. and J.H.B. are at Cambridge Display Technology, 181A Huntingdon Road, Cambridge CB3 0DJ, UK. R.N.M. and C.T. are at the Istituto di Spettroscopia Molecolare, CNR, Via Gobetti, 101, 40129 Bologna, Italy. D.D.C.B. is at the Department of Physics, University of Sheffield, Sheffield S3 7RH, UK. D.A.D.S. and J.L.B. are at the Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc, 20, B-7000 Mons, Belgium. M.L. and W.R.S. are at the Department of Physics, Linköping University, S-58183 Linköping, Sweden.

---

1. Pope, M., Kallmann, H. & Magnante, P. Electroluminescence in organic crystals. *J. Chem. Phys.* **38,** 2042–2043 (1963).
2. Helfrich, W. & Schneider, W. G. Recombination radiation in anthracene crystals. *Phys. Rev. Lett.* **14,** 229–231 (1965).
3. Tang, C. W. & Van Slyke, S. A. Organic electroluminescent diodes. *Appl. Phys. Lett.* **51,** 913–915 (1987).
4. Adachi, C., Tsutsui, T. & Saito, S. Organic electroluminescent device having a hole conductor as an emitting layer. *Appl. Phys. Lett.* **55,** 1489–1491 (1989).
5. Chiang, C. K. *et al.* Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.* **39,** 1098–1101 (1977).
6. Garnier, F., Hajlaoui, R., Yassar, A. & Srivastava, P. All-polymer field-effect transistor realized by printing techniques. *Science* **265,** 1684–1686 (1994).
7. Ostoja, P. *et al.* Electrical characteristics of field-effect transistors formed with ordered alpha-sexithienyl. *Synth. Met.* **54,** 447–452 (1993).
8. Torsi, L., Dodabalapur, A., Rothberg, L. J., Fung, A. W. P. & Katz, H. E. Intrinsic transport-properties and performance limits of organic field-effect transistors. *Science* **272,** 1462–1464 (1996).
9. Yang, Y. & Heeger, A. J. A new architecture for polymer transistors. *Nature* **372,** 344–346 (1994).
10. Brown, A. R., Pomp, A., Hart, C. M. & Deleeuw, D. M. Logic gates made from polymer transistors and their use in ring oscillators. *Science* **270,** 972–974 (1995).
11. Sirringhaus, H., Tessler, N. & Friend, R. H. Integrated optoelectronic circuits based on conjugated polymers. *Science* **280,** 1741–1744 (1998).
12. Yu, G., Gao, J., Hummelen, J. C., Wudl, F. & Heeger, A. J. Polymer photovoltaic cells—enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science* **270,** 1789–1791 (1995).
13. Granström, M. *et al.* Laminated fabrication of polymeric photovoltaic diodes. *Nature* **395,** 257–260 (1998).
14. Burroughes, J. H. *et al.* Light-emitting diodes based on conjugated polymers. *Nature* **347,** 539–541 (1990).
15. Burn, P. L. *et al.* Chemical tuning of electroluminescent copolymers to improve emission efficiencies and allow patterning. *Nature* **356,** 47–49 (1992).
16. Greenham, N. C., Moratti, S. C., Bradley, D. D. C., Friend, R. H. & Holmes, A. B. Efficient polymer-based light-emitting diodes based on polymers with high electron affinities. *Nature* **365,** 628–630 (1993).
17. Braun, D. & Heeger, A. J. Visible light emission from semiconducting polymer diodes. *Appl. Phys. Lett.* **58,** 1982–1984 (1991).
18. Gustafsson, G. *et al.* Flexible light-emitting diodes made from soluble conducting polymers. *Nature* **357,** 477–479 (1992).
19. Greenham, N. C. & Friend, R. H. in *Solid State Physics* (eds Ehrenreich, H. & Spaepen, F. A.) 2–150 (Academic, San Diego, USA, 1995).
20. Salbeck, J. Electroluminescence with Organic Compounds. *Ber. Bunsenges. Phys. Chem.* **100,** 1667–1677 (1996).
21. Sheats, J. R. *et al.* Organic electroluminescent devices. *Science* **273,** 884–888 (1996).
22. Kraft, A., Grimsdale, A. C. & Holmes, A. B. Electroluminescent conjugated polymers—seeing polymers in a new light. *Angew. Chem. Int. End Engl.* **37,** 402–428 (1998).
23. Grüner, J., Cacialli, F. & Friend, R. H. Emission enhancement in single-layered conjugated polymer microcavities. *J. Appl. Phys.* **80,** 207–215 (1996).
24. Liedenbaum, C., Croonen, Y., van de Weijer, P., Vleggaar, J. & Schoo, H. Low voltage operation of large area polymer LEDs. *Synth. Met.* **91,** 109–111 (1997).
25. Spreitzer, H. *et al.* Soluble phenyl-substituted PPVs—New materials for highly efficient polymer LEDs. *Adv. Mater.* **10,** 1340–1344 (1998).
26. Lacey, D. High-efficiency polymer light-emitting diodes. 9th International Workshop on Inorganic and Organic Electroluminesence, Oregon, Bend, USA, September 13–17, 1998. See also ⟨http: www.cdtltd.co.uk⟩
27. Brown, A. R. *et al.* Poly(p-phenylene vinylene) light-emitting diodes: enhanced electroluminescence efficiency through charge carrier confinement. *Appl. Phys. Lett.* **61,** 2793–2795 (1992).
28. Salaneck, W. R. & Brédas, J. L. The metal-on-polymer interface in polymer light-emitting-diodes. *Adv. Mater.* **8,** 48–52 (1996).
29. Salaneck, W. R., Stafström, S. & Brédas, J. L. *Conjugated Polymer Surfaces and Interfaces* (Cambridge Univ. Press, 1996).
30. Brédas, J. L. Conjugated polymers and oligomers—designing novel materials using a quantum-chemical approach. *Adv. Mater.* **7,** 263–274 (1995).
31. Johansson, N. *et al.* A study of the ITO-on-PPV interface using photoelectron spectroscopy. *Synth. Met.* **92,** 207–211 (1998).
32. Logdlund, M. & Brédas, J. L. Theoretical-studies of the interaction between aluminum and poly(p-phenylenevinylene) and derivatives. *J. Chem. Phys.* **101,** 4357–4364 (1994).
33. Dannetun, P. *et al.* Interface formation between poly(2,5-diheptyl-p-phenylenevinylene) and calcium—implications for light-emitting diodes. *Synth. Met.* **67,** 133–136 (1994).
34. Gao, Y., Park, K. T. & Hsieh, B. R. Interface formation of Ca with poly(*p*-phenylene vinylene). *J. Appl. Phys.* **73,** 7894–7899 (1993).
35. Hung, L. S., Tang, C. W. & Mason, M. G. Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode. *Appl. Phys. Lett.* **70,** 152–154 (1997).
36. Bröms, P., Birgersson, J., Johansson, N., Logdlund, M. & Salaneck, W. R. Calcium electrodes in polymer LEDs. *Synth. Met.* **74,** 179–181 (1995).
37. Hayashi, S., Etoh, H. & Saito, S. Electroluminescence of perylene films with a conducting polymer as an anode. *Jpn J. Appl. Phys.* **25,** 773–775 (1986).
38. Nakano, T., Doi, S., Noguchi, T., Ohnishi, T. & Iyechika, Y. Organic electroluminescent device. US Patent 5,317,169 (1994).
39. Yang, Y. & Heeger, A. J. Polyaniline as a transparent electrode for polymer light-emitting diodes: lower operating voltage and higher efficiency. *Appl. Phys. Lett.* **64,** 1245–1247 (1994).
40. Karg, S., Scott, J. C., Salem, J. R. & Angelopoulos, M. Increased brightness and lifetime of polymer light-emitting-diodes with polyaniline anodes. *Synth. Met.* **80,** 111–117 (1996).
41. Carter, J. C. *et al.* Operating stability of light-emitting polymer diodes based on poly(p-phenylene vinylene). *Appl. Phys. Lett.* **71,** 34–36 (1997).
42. Pei, Q. B., Yu, G., Zhang, C., Yang, Y. & Heeger, A. J. Polymer light-emitting electrochemical-cells. *Science* **269,** 1086–1088 (1995).
43. de Mello, J. C., Tessler, N., Graham, S. C. & Friend, R. H. Ionic space-charge effects in polymer light-emitting diodes. *Phys. Rev. B* **57,** 12951–12963 (1998).
44. Gao, J., Yu, G. & Heeger, A. J. Polymer light-emitting electrochemical cells with frozen p-i-n junction. *Appl. Phys. Lett.* **71,** 1293–1295 (1997).
45. Campbell, I. H., Hagler, T. W., Smith, D. L. & Ferraris, J. P. Direct measurement of conjugated polymer electronic excitation-energies using metal/polymer/metal structures. *Phys. Rev. Lett.* **76,** 1900–1903 (1996).
46. Marks, R. N., Bradley, D. D. C., Jackson, R. W., Burn, P. L. & Holmes, A. B. Charge injection and transport in poly(p-phenylene vinylene) light-emitting-diodes. *Synth. Met.* **57,** 4128–4133 (1993).
47. Parker, I. D. Carrier tunneling and device characteristics in polymer light-emitting-diodes. *J. Appl. Phys.* **75,** 1656–1666 (1994).
48. Blom, P. W. M., De Jong, M. J. M. & Vleggaar, J. J. M. Electron and hole transport in poly(p-phenylene vinylene) devices. *Appl. Phys. Lett.* **68,** 3308–3310 (1996).
49. Davids, P. S., Kogan, S. M., Parker, I. D. & Smith, D. L. Charge injection in organic light-emitting-diodes—tunneling into low mobility materials. *Appl. Phys. Lett.* **69,** 2270–2272 (1996).
50. Conwell, E. M. & Wu, M. W. Contact injection into polymer light-emitting diodes. *Appl. Phys. Lett.* **70,** 1867–1869 (1997).
51. Bassler, H. Injection, transport and recombination of charge carriers in organic light-emitting diodes. *Polym. Adv. Technol.* **9,** 402–418 (1998).
52. Blom, P. W. M., de Long, M. J. & van Munster, M. G. Electric-field and temperature dependence of the hole mobility in poly(p-phenylene vinylene). *Phys. Rev. B* **55,** 1–3 (1997).
53. Blom, P. W. M., de Jong, M. J. M. & Breedijk, S. Temperature dependent electron-hole recombination in polymer light-emitting diodes. *Appl. Phys. Lett.* **71,** 930–932 (1997).
54. Tang, C. W., Van Slyke, S. A. & Chen, C. H. Electroluminescence of doped organic thin films. *J. Appl. Phys.* **65,** 3610–3616 (1989).
55. Shi, J. M. & Tang, C. W. Doped organic electroluminescent devices with improved stability. *Appl. Phys. Lett.* **70,** 1665–1667 (1997).
56. Baigent, D. R. *et al.* Light-emitting diodes fabricated with conjugated polymers—recent progress. *Synth. Met.* **67,** 3–10 (1994).
57. Becker, H., Burns, S. E. & Friend, R. H. The effect of metal films on the photoluminescence and electroluminescence of conjugated polymers. *Phys. Rev. B* **56,** 1893–1905 (1997).
58. Scott, J. C., Karg, S. & Carter, S. A. Bipolar charge and current distributions in organic light-emitting diodes. *J. Appl. Phys.* **82,** 1454–1460 (1997).

59. Swanson, L. S. *et al.* Electroluminescence-detected magnetic-resonance study of polyparaphenylene-vinylene (PPV)-based light-emitting diodes. *Phys. Rev. B* **46,** 15072–15077 (1992).
60. Brown, A. R. *et al.* Optical spectroscopy of triplet excitons and charged excitations in poly(p-phenylenevinylene) light-emitting diodes. *Chem. Phys. Lett.* **210,** 61–66 (1993).
61. Baldo, M. A. *et al.* Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* **395,** 151–154 (1998).
62. Cleave, V. M., Yahioglu, G., Le Barny, P., Friend, R. H. & Tessler, N. Harvesting of singlet and triplet energy in polymer LEDs. *Adv. Mater.* (in the press).
63. Soos, Z. G., Galvao, D. S. & Etemad, S. Fluorescence and excited-state structure of conjugated polymers. *Adv. Mater.* **6,** 280–287 (1994).
64. Chandross, M. *et al.* Excitons in poly(para-phenylenevinylene). *Phys. Rev. B* **50,** 14702–14705 (1994).
65. Brédas, J. L., Cornil, J. & Heeger, A. J. The exciton binding-energy in luminescent conjugated polymers. *Adv. Mater.* **8,** 447–452 (1996).
66. Alvarado, S. F., Seidler, P. F., Lidzey, D. G. & Bradley, D. D. C. Direct determination of the exciton binding energy of conjugated polymers using a scanning tunneling microscope. *Phys. Rev. Lett.* **81,** 1082–1085 (1998).
67. Greenham, N. C. *et al.* Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers. *Chem. Phys. Lett.* **241,** 89–96 (1995).
68. Cornil, J., dos Santos, D. A., Crispin, X., Silbey, R. & Brédas, J. L. Influence of interchain interactions on the absorption and luminescence of conjugated oligomers and polymers: a quantum-chemical characterization. *J. Am. Chem. Soc.* **120,** 1289–1299 (1998).
69. Samuel, I. D. W., Rumbles, G. & Collison, C. J. Efficient interchain photoluminescence in a high-electron-affinity conjugated polymer. *Phys. Rev. B* **52,** 11573–11576 (1995).
70. Rothberg, L. J. *et al.* Photophysics of phenylenevinylene polymers. *Synth. Met.* **80,** 41–58 (1996).
71. Harrison, N. T., Hayes, G. R., Phillips, R. T. & Friend, R. H. Singlet intrachain exciton generation and decay in poly(p-phenylene vinylene). *Phys. Rev. Lett.* **77,** 1881–1884 (1996).
72. Muccini, M. *et al.* Polarized fluorescence in alpha-sexithienyl single crystal at 4.2 K. *J. Chem. Phys.* **108,** 7327–7333 (1998).
73. Gill, R. E., Meetsma, A. & Hadziioannou, G. Two novel thermotropic liquid-crystalline substituted oligo(p-phenylene-vinylene)s—single-crystal x-ray determination of an all-trans oligomeric PPV. *Adv. Mater.* **8,** 212–218 (1996).
74. Chance, R. R., Prock, A. & Silbey, R. in *Advances in Chemical Physics* (eds Prigogine, I. & Rice, S. A.) 1–65 (Wiley, New York, 1978).
75. Tsutsui, T., Takada, N., Saito, S. & Ogino, E. Sharply directed emission in organic electroluminescent diodes with an optical-microcavity structure. *Appl. Phys. Lett.* **65,** 1868–1870 (1994).
76. Jordan, R. H., Rothberg, L. J., Dodabalapur, A. & Slusher, R. E. Efficiency enhancement of microcavity organic light-emitting-diodes. *Appl. Phys. Lett.* **69,** 1997–1999 (1996).
77. Fisher, T. A. *et al.* Electroluminescence from a conjugated polymer microcavity structure. *Appl. Phys. Lett.* **67,** 1355–1357 (1995).
78. Lemmer, U. *et al.* Microcavity effects in a spin-coated polymer 2-layer system. *Appl. Phys. Lett.* **66,** 1301–1303 (1995).
79. Tessler, N., Denton, G. J. & Friend, R. H. Lasing in conjugated polymer microcavities. *Nature* **382,** 695–697 (1996).
80. Tessler, N., Harrison, N. T. & Friend, R. H. High peak brightness polymer light-emitting diodes. *Adv. Mater.* **10,** 64–68 (1998).
81. Lidzey, D. G., Bradley, D. D. C., Alvarado, S. F. & Seidler, P. F. Electroluminescence in polymer films. *Nature* **386,** 135 (1997).
82. Beljonne, D., Shuai, Z., Friend, R. H. & Brédas, J. L. Theoretical investigation of the lowest singlet and triplet states in poly(para phenylene vinylene) oligomers. *J. Chem. Phys.* **102,** 2042–2049 (1995).
83. Wakimoto, T. *et al.* Stability characteristics of quinacridone and coumarin molecules as guest dopants in the organic LEDs. *Synth. Met.* **91,** 15–19 (1997).
84. Hosokawa, C. *et al.* Organic multi-color electroluminescence display with fine pixels. *Synth. Met.* **91,** 3–7 (1997).
85. Miyaguchi, S. *et al.* OLED full-color passive matrix display. 9th International Workshop on Inorganic and Organic Electroluminesence, Oregon, Bend, USA, September 13–17, 1998.
86. Scurlock, R. D., Wang, B. J., Ogilby, P. R., Sheats, J. R. & Clough, R. L. Singlet oxygen as a reactive intermediate in the photodegradation of an electroluminescent polymer. *J. Am. Chem. Soc.* **117,** 10194–10202 (1995).
87. Xing, K. Z. *et al.* The interaction of poly(p-phenylene-vinylene) with air. *Adv. Mater.* **8,** 971–974 (1996).
88. Burrows, P. E. *et al.* Reliability and degradation of organic light-emitting devices. *Appl. Phys. Lett.* **65,** 2922–2944 (1994).
89. Hebner, T. R., Wu, C. C., Marcy, D., Lu, M. H. & Sturm, J. C. Ink-jet printing of doped polymers for organic light emitting devices. *Appl. Phys. Lett.* **72,** 519–521 (1998).
90. Bharathan, J. & Yang, Y. Polymer electroluminescent devices processed by inkjet printing: I. Polymer light-emitting logo. *Appl. Phys. Lett.* **72,** 2660–2662 (1998).
91. Burn, P. L. *et al.* Precursor route chemistry and electronic properties of poly(1,4-phenylenevinylene), poly(2,5-dimethyl-1,4-phenylenevinylene), and poly(2,5-dimethoxy-1,4-phenylenevinylene). *J. Chem. Soc. Perkin Trans 1* 3225–3231 (1992).
92. Remmers, M. *et al.* The optical, electronic, and electroluminescent properties of novel poly(p-phenylene)-related polymers. *Macromolecules* **29,** 7432–7445 (1996).
93. Scherf, U. & Müllen, K. A soluble ladder polymer via bridging of functionalised poly(p-phenylene)-precursors. *Makromol. Chem. Rapid Commun.* **12,** 489–797 (1991).
94. Yang, Y. *et al.* Efficient blue polymer light-emitting-diodes from a series of soluble poly(paraphenylene)s. *J. Appl. Phys.* **79,** 934–939 (1996).
95. Birgerson, J. *et al.* Efficient blue-light emitting devices from conjugated polymer blends. *Adv. Mater.* **8,** 982–985 (1996).
96. Klarner, G., Davey, M. H., Chen, W. D., Scott, J. C. & Miller, R. D. Colorfast blue-light-emitting random copolymers derived from di-n- hexylfluorene and anthracene. *Adv. Mater.* **10,** 993–999 (1998).
97. Janietz, S. *et al.* Electrochemical determination of the ionization potential and electron affinity of poly(9,9-dioctylfluorene). *Appl. Phys. Lett.* **73,** 2453–2455 (1998).

Acknowledgements. We thank the European Commission (ESPRIT programme 8013 LEDFOS) for support. Research in Mons is partly supported by the Belgian Federal Government (Pôle d'Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse), FRNS-FRFC, and an IBM Academic Joint Study.

Correspondence should be addressed to R.H.F. at the University of Cambridge (e-mail: rhf10@cam.ac.uk).