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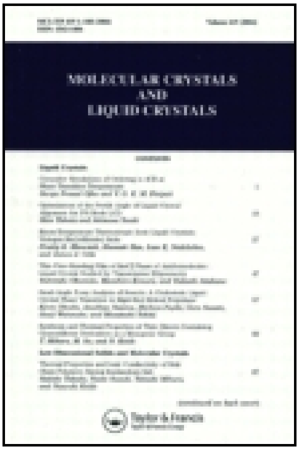

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Electroluminescence of Organic Thin Films Leading to Light Emitting Molecular Devices

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ELECTROLUMINESCENCE OF ORGANIC THIN FILMS LEADING TO LIGHT EMITTING MOLECULAR DEVICES

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Abstract The factors affecting the efficiency and lifetime of organic electroluminescent devices are reviewed and illustrated with reference to work carried out in the author's laboratory as well as describing recent developments in organic heterojunction and polymer systems.

INTRODUCTION

Light emitting diodes (LED) have been readily available for many years, although their spectral range has been limited until recently. Even now, commercially available blue diodes have poor efficiencies. LED are also limited by the single-crystal technology used for their production, so that there is little scope for making large-area displays.

Inorganic large-area displays have been made from compound semiconductors such as zinc sulphide, either as polycrystalline films or as particles dispersed in a resistive binder; panels using organic phosphors have been made on this last principle. This paper, however, will be exclusively concerned with the electroluminescence (EL) of thin films of polycrystalline organic materials and polymers.

It is over a quarter of a century since electroluminescence was first observed in thin crystals of anthracene[1]. The general mechanism was established as double injection followed by recombination; ie, electrons were injected into the conduction band at the cathode contact, holes were injected at the anode, and somewhere in the bulk of the material, recombination took place, with emission of light characteristic of the fluorescence spectrum of the anthracene, ie in the blue-violet region of the spectrum. The original work made use of liquid contacts, and two later inventions were needed before credible devices could be made: the introduction of solid electrodes[2], and the demonstration that thin evaporated films would also electroluminesce[3].

In our own laboratories, we showed that many different organic materials gave electroluminescence, and that appreciable light could be generated even at low voltages[4], and with a range of colours depending on the emitting molecule.

This paper will qualitatively describe the mechanism of charge injection and luminescence of organic molecular thin film electroluminescent devices, and will describe some further results obtained in this laboratory. Particular attention will be given to two of the key features determining the eventual viability of organic EL devices: the efficiency and the lifetime. The area has become very active recently, and some of the key new literature will be reviewed.

MECHANISM OF CARRIER INJECTION AND RECOMBINATION

It is often assumed that conduction processes in organic molecular materials such as those discussed here can be described by a band model. The distinction between band and hopping conduction in a molecular solid will depend on the overlap of the Pi orbitals of the individual molecules in the crystal structure, higher overlaps being conducive to band type behaviour. It seems probable that some of the materials examined would better be described by a hopping model, especially as thin evaporated films will have a wide range of crystal orientations, including ones with little orbital overlap in the field direction.

For most of the discussion, the band model will be used, as it provides a good qualitative insight into the processes taking place. It must not be forgotten, however, that the bands are much narrower than those common in inorganic semiconductors, and that the wide bandgap and absence of electronic doping mean that the equilibrium concentration of carriers and the bulk conductivity are very low.

The overall process will be described in relation to anthracene, which was the first organic electroluminescent material to be investigated. The band structure of anthracene is shown in Figure 1. The band gap is about 4.0 eV and the conduction and valence bands are less than 0.1 eV wide, because of the relatively weak interaction between molecules. The conduction band is located at about 1.6 eV below the vacuum level. In addition to the band structure there are two excitonic states which are of relevance; there is a charge transfer (CT) exciton, which can be described as a pair of anthracene molecules one of which carries a hole, and one an electron; this is located at 3.4 eV above the valence band. There is also a singlet exciton, which is analogous to an electronically excited anthracene molecule, and is located at 3.1 eV above the valence band[5]. Both these species are mobile and can travel over several nm during their lifetimes. Triplet CT and neutral excitons also exist, but are significant only as a competitive path to EL.

There are also many trapping states, which have been studied in single crystals[6], but are less well characterised in polycrystalline films. They arise because of defects in the structure (grain boundaries between the crystallites etc), and chemical impurities, which are either present in the starting materials or are formed during operation of the device.

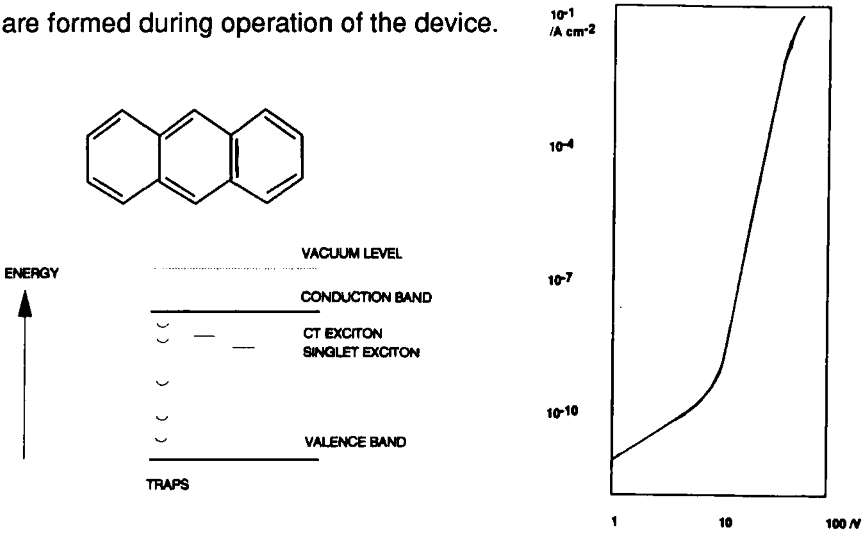


FIGURE 1: Chemical and band structures and I/V characteristics of anthracene.

Because of the large band gap, the concentration of carriers is low enough to make bulk anthracene a good insulator (>10^{16} ohm cm resistivity), and in the absence of doping, any carriers must be injected from the electrodes. In the course of this they build up a space charge, and the behaviour that is seen in the thin anthracene films is characteristic of space charge limited conduction.

Gold provides an efficient hole injection electrode; we studied a number of samples based on a sandwich structure consisting of a gold bottom electrode deposited onto a glass slide, anthracene deposited on top of the gold, with a top electrode also of gold. These samples exhibited typically a 10:1 ratio of rectification, with the top electrode acting as a more efficient hole injector; this was believed to be due to superior contact of the upper electrode, and possibly also to partial penetration of the organic layer by gold whiskers. Often a sample when first made would appear to be short-circuited, but application of a brief high current through a limiting resistor of a few hundred ohms would clear the short and allow the properties of the structure to be studied; this behaviour is consistent with penetration of the organic layer by the gold.

Most samples showed a current/voltage typical of space charge limited behaviour as the applied voltage was raised. Initially the current rose almost linearly with voltage, and then entered a region in which the current had a power law dependence on the voltage, with the power typically in the region of 6-12, depending on the nature of the sample and the electrodes. A typical plot of current against voltage is shown in Figure 1. The power law dependence is consistent with space charge limitation of the current, and hints at an exponential distribution of traps[7].

Electrons were injected from an aluminium or magnesium electrode; the work functions of these metals are not sufficiently low for direct injection into the conduction band of anthracene, so some field assisted tunneling or other process must have been a necessary part of the electron injection. Once there are a significant number of holes and electrons injected into the organic layer, the equilibrium carrier concentration will be substantially exceeded, and recombination will take place. The distribution of charge within the layer is expected to be highly nonuniform, with high concentrations of charge carriers near the electrodes. The recomination process is not direct, but involves prior formation of a CT exciton and then a singlet exciton, as in Figure 2.

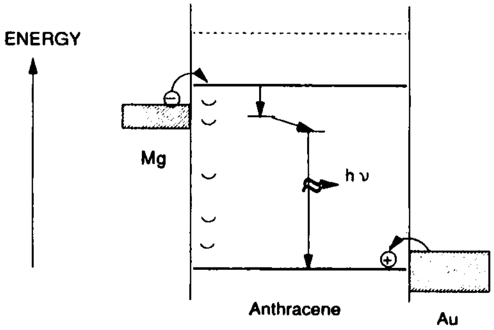


FIGURE 2 Electroluminescence of Anthracene

Typical EL samples were made (for experimental details see Reference 4) by vacuum deposition of an aluminium or magnesium layer onto a glass substrate, followed by the organic layer, with a final layer of gold, which was sufficienly thin to be partially transparent to the EL (Figure 3). In order to protect the samples against degradation by oxygen or moisture, they were examined under nitrogen, in a glove box or after encapsulation .

FACTORS AFFECTING ELECTROLUMINESCENT EFFICIENCY

The final efficiency with which light is emitted can be measured as a *quantum yield* Φ_{EL}or as a *power efficiency.* The quantum yield is the number of photons emitted for each electron that is transported through the device, the power efficiency is simply the ratio between the electrical input power and the radiated light power. It therefore depends on the voltage drop across the device. If the voltage drop is V volts and the energy of the radiation is v eV, then the power efficiency, $E_{EL} = \Phi_{EL} \times v/V$.

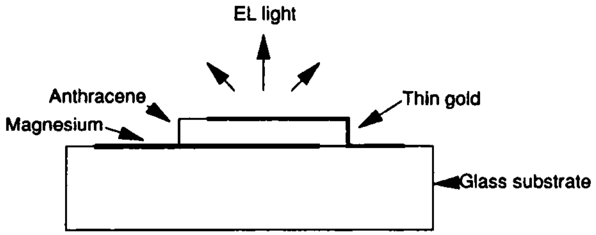


FIGURE 3 **Structure of electroluminescent samples.**

It is useful to break down the components of these efficiencies, as it provides an insight into the limiting processes , and also provides some clues about factors that may affect the lifetime.

Injection, Transport and Recombination

The injection process itself will account for some of the voltage drop across the device, but the most likely mechanism for limiting the efficiency is the tendency for an imbalance between hole and electron injection. Depending upon the nature of the EL material, it is likely that either holes or electrons are injected in excess; the excess carriers will transport current through the material without being able to contribute to the emission of light, and can therefore severely limit Φ_{EL}. This limitation is potentially an important one, as the ratio betwen the two types of carriers can be very large.

There will be an inevitable voltage drop across the organic layer, significantly reducing the E_{EL}. Better conducting materials and thinner films will have a lower voltage drop; conversely, the presence of trapped charge carriers will cause an increase. As we are dealing with polycrystalline or amorphous films, there is likely to be a high concentration of trapped charge.

Because of the low dielectric constant and poor screening in organic molecules, it is likely that recombination will be fairly efficient; the potential well created around a carrier will extend for several lattice spacings and will attract carriers of the opposite sign. Trapped charges will also behave in a similar way, and will not necessarily lead to singlet excitons[8].

Generation of a Singlet Exciton

When the two oppositely charged carriers recombine they may form either a singlet or a triplet charge transfer exciton. The probability of formation of a singlet exciton has been estimated as[9] 0.25, although, as the figure is kinetically determined[10], it is possible that more favourable statistics might prevail if recomination is fast. It is likely that the charge transfer excitons will relax to the corresponding singlet or triplet excitons very efficiently. As the lifetime of triplet excitons is relatively long, they can also contribute to the formation of singlet excitons by a triplet-triplet annihilation process.

The efficiency of emission of light from the singlet excitons will firstly depend on the fluorescence quantum yield Φ_F of the organic material. Although there have been extensive surveys of Φ_F in solution, there is less information available for single crystals, and some degree of certainty that the evaporated film value will be rather different, depending on the method of preparation. Anthracene crystals are known to have a very high Φ_F, but the mobility of the singlet excitons makes them vulnerable to quenching processes. If the anthracene contains impurities with singlet energies lower than 3.1 eV, energy can be transferred to the impurity, which in appropriate cases can luminesce[11], thus allowing a mechanism for emission of light of longer wavelength. Most impurities will not have high Φ_F values, and will simply provide a route for radiationless decay. The electrode surfaces are particularly important regions for singlet exciton deactivation, as metals in particular quench singlet excitons very efficiently[12]. In view of the high concentrations of free and trapped carriers in the vicinity of the electrodes, this may be one of the most important limitations on the efficiency of the simple structures discussed so far. Singlet excitons are also vulnerable to deactivation by electron transfer either at the electrodes or at impurity sites in the material.

Escape of Light from the Device

In order to be observed and measured, the light emitted by radiative decay of singlet excitons must escape from the device. This requires the presence of a transparent electrode; in the case of the gold electrodes the transmission was typically about 20%. The use of transparent conducting oxide electrodes provides an obvious way of improving this, provided that efficient carrier injection can be retained.

FACTORS AFFECTING LIFETIME

Any practical device will be required to have a working lifetime (depending on application), of at least 10,000 hours. Various factors can potentially reduce the efficiency of the devices over the course of time. Many of these factors are directly mediated by atmospheric oxygen and water vapour, and can be inhibited by hermetic encapsulation, which was the reason that our measurements were made under dry nitrogen in a glove box or a glass-encapsulated system. Nevertheless, it is difficult to ensure total exclusion of oxygen and water vapour, and any residues or leakage will cause degradation of the device.

Degradation of the Electrodes

The electron injecting electrode is typically made of a low work function metal; in the case that this is aluminium, it forms a protective oxide layer that is, to some extent, self limiting. Magnesium, however, continues to oxidise indefinitely. We found that for many EL materials, magnesium was a much better electron injector than aluminium (this is consistent with the work function difference between the metals), but that slow degradation of the metal surface occurred even in encapsulated samples. VanSlyke[13] has observed a similar degradation of magnesium alloy cathodes, and has proposed a multilayer structure with a codeposited (aluminium and organic) top layer to protect the electrode.

The nature of the cathode surface is, of course critical to efficient carrier injection (particularly in the case of electrons), and degradation usually leads to dark spots, where injection has become inefficient relative to the rest of the surface. As time goes on, electron injection can become almost totally suppressed over the whole surface.

Degradation of the Electroluminescent Layer

Perhaps the most basic form of degradation is the gradual ageing process by which larger crystallites in a polycrystalline film grow at the expense of the smaller ones. This is an example of Ostwald type ripening, and depends on the vapour pressure of the organic material concerned. We have shown that this factor effectively excludes anthracene from use as a stable EL material, but that larger molecules can have adequate stability[14].

The singlet exciton state is particularly vulnerable to impurities because of the ready transfer of electronic energy or electrons, and because of its mobility. Thus any impurities which are formed during the life of the device can have a dramatic effect on the Φ_{EL}.

How do these impurities form? It must be remembered that the species involved in EL processes are highly reactive chemically, and that it is therefore not surprising that adventitious water or oxygen will undergo reactions. In some cases the species are capable of undergoing reaction without involvement of any impurity molecule.

The emitting state itself (the singlet exciton) represents an excess energy of 3 eV that is localised over a few molecules, and can effectively become available to any of them, so that as a first approximation it can be regarded as an electronically excited anthracene molecule. Singlet excited anthracene is well known to react not only with impurities, but also with itself to give dimers. These dimers will not form within ordered regions of the crystal, because the molecules are not in an appropriate spatial arrangement. However, there will be reaction centres at the grain boundaries, and dimers will form there. The dimers themselves have a singlet energy greater than that of the anthracene singlet exciton, and are therefore unlikely to cause quenching. However, they inevitably cause further disruption of the crystalline order and cause growth of defects.

The charge carriers (holes and electrons) can similarly be regarded as perturbed anthracene radical cations and anions. These species can be prepared chemically in solution (where solvation effects increase their stability). They have to be made under careful exclusion of oxygen and moisture, and react rapidly with a wide variety of other species. It is hardly surprising that the similar species in the solid state are susceptible to chemical attack.

Less dramatic effects due to the charge carriers are seen as slowly reversible trapping. The current in an EL sample will gradually decrease over the course of time, and the light emission will show a similar decrease. Some of this can be recovered by leaving the sample to recover for a period of days or weeks, or by applying a voltage in the inverse direction for shorter periods. Big reductions in the rate of decay of samples were gained by using either a sine wave alternating voltage, or preferably, an appropriate combination of positive and negative pulses to drive the EL sample. Nevertheless, the reversible trapping was only part of the overall degradation.

ELECTROLUMINESCENCE OF PERYLENE, BENZPERYLENE AND DICHLOROPERYLENE AND OTHER ORGANICS

It was indicated in our earlier work (Reference 4), that perylene and benzperylene had given similar results to anthracene.

Perylene

Perylene (Figure 4a) was initially chosen for study because the conduction band was more accessible than in the case of anthracene, and because of a critical difference in crystal structure. In perylene, the molecules are arranged in pairs with sufficient overlap to lead to excimer formation[15]. Thus the fluorescence of perylene crystals is a yellow colour, showing a large shift from the blue fluorescence of perylene in dilute solution.

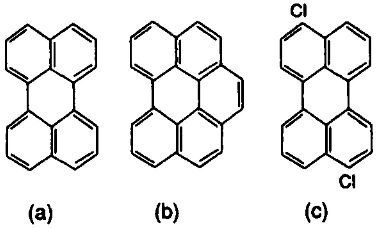


FIGURE 4 (a) Perylene, (b) Benzperylene and (c) anthracene.

This excimer formation means that the excitation is much less mobile than in the case of an anthracene singlet exciton, and has been measured[16] to have a diffusion coefficient of 3 x 10^{-3} cm^2 s^{-1}. This figure was not available at the time of the work, but the expectation of low exciton mobility encouraged the study of perylene as it was expected to be less susceptible than anthracene to impurity quenching, even though the basic Φ_F was only about 0.3.

In practice, the maximum Φ_{EL} was very similar to that of anthracene (about 0.01%), although there were detailed differences in the behaviour of the two materials. For example, aluminium and magnesium were very similar in terms of electron injecting efficiency into anthracene, whereas magnesium was an order of magnitude better for perylene. The lifetime of perylene devices was much better than that of anthracene, with a half life typically measured in hours rather than minutes. Part of the difference may be ascribed to the relative immunity of perylene to the ripening process referred to earlier, and part to the relatively more robust nature of the molecule and the low singlet exciton mobility.

The voltage drop, with its consequent effect on power efficiency was broadly similar for the two materials, and was subject to a trade off. Thick (1-2 μm) EL layers tended to give the highest values of Φ_{EL}, but had a high voltage drop, which reduced the power efficiency. Thin layers (< 0.4 μm) were difficult to prepare without internal short circuits (ascribed to gold whiskers), and also tended to give low Φ_{EL} values (presumably because electrode quenching effects became more dominant). Layers of about 0.5 μm typically gave a voltage drop of 20-30 V, and therefore represented an order of magnitude difference between E_{EL} and Φ_{EL}.

Another consequence of the molecular pairing in the perylene structure is the reduction of carrier drift mobility from about 1 $cm^2 V^{-1} s^{-1}$ for anthracene to about 10^{-3} $cm^2 V^{-1} s^{-1}$ for perylene[17]. It is interesting that this clear transition from band conduction to hopping conduction has had no obvious consequences for the conduction and EL behaviour.

Benzperylene

Benzperylene (Figure 4b) was chosen for study because it had a relatively (to anthracene) accessible conduction band, and a high Φ_F; it also had a low vapour pressure at room temperature, thus avoiding the ripening process. It does not have a dimeric crystal structure giving excimer fluorescence.

The electrical properties of the films were similar to those of anthracene and perylene. The EL colour was a turquoise blue, consistent with the photoluminescence, but the Φ_{EL} was a factor of 5 higher, at 0.05%, corresponding to an internal efficiency of 0.2% after allowing for transmission losses in the gold electrode. Benzperylene devices tended to be much more stable than either anthracene or perylene, and the best device gave a half life of 800 hours when operated at an intensity easily visible in a darkened room. There was a large scatter in the observed lifetime of nominally identical devices, and all the devices showed much shorter half lives at higher intensities.

Dichloroperylene etc

The structure of one isomer of dichloroperylene is shown in Figure 4c; this material was synthesised in the hope that the electronegativity of the chlorine atoms would reduce the energy of the conduction band and allow more efficient electron injection. Unfortunately, the Φ_F was found to be low, so that the overall Φ_{EL} was low. The electrical characteristics were curious, indicating two distinct sets of traps.

A wide range of other organic EL layers was examined, with particular emphasis on molecules containing heteroatoms and therefore presumed to have a higher electron affinity. None was found to give higher Φ_{EL} than benzperylene.

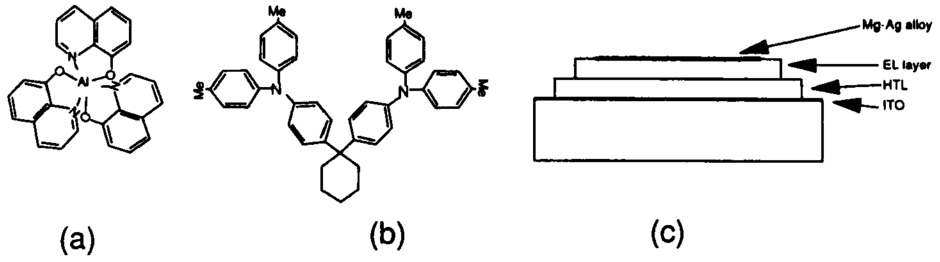
ORGANIC HETEROJUNCTION DEVICES

We made devices in which a thin layer of either perylene or benzperylene was deposited onto magnesium, followed by a thicker layer of benzperylene and a transparent gold electrode. The object of this was to improve the efficiency of the electron injection process by making use of the lower conduction band energies of the first two materials. When a 30 nm layer of perylene was used as the first layer, followed by a 500 nm layer of benzperylene, the observed electroluminescence showed spectral characteristics indicating that light emission was occurring from both species.

An electron injection layer of only 16 nm of dichloroperylene was enough to ensure that the EL spectrum was characteristic only of the dichloroperylene. These two results are consistent with a view that the electrical characteristics of the device were being dominated by the hole transport process, but that EL was dominated by electron injection and transport. Hayashi et al[18] also observed that EL tended to be localised near to the cathode.

Addition of Hole Transport Layers

A major step forward in device efficiency was achived by Tang and VanSlyke[19], who used an EL layer of an aluminium trisoxine complex (Figure 5a) in conjunction with a *hole transport layer* (Figure 5b). The electronegativity of the complex is much greater than that of the aromatic hydrocarbons discussed above, and consequently, electron injection is a much easier process, using a top electrode of magnesium/silver alloy, and a conductive glass anode; the device structure is shown in Figure 5c. We had previously attempted to use magnesium top electrodes with either gold or conductive glass anodes, but had obtained poor and irreproducible electrode properties; alloying with silver seems to be a significant factor in obtaining a good top contact.



(a) (b) (c)

FIGURE 5 (a) EL layer, (b) HTL, and (c) device structure.

The hole transport layer (HTL) is a concept that has been taken from electrophotography. It provides a good interface with the anode, and readily transports holes to the organic heterojunction. It is probable that recombination and emission occur in this region, and that the relatively high $\Phi_{EL}$of this type of device (the reference quotes a value of 1%), is due to good balance of electron and hole injection, and the isolation of the emitting region from the electrodes. The importance of avoiding exciplex formation between the HTL and EL layers has been stated[20], and is consistent with the above discussion on the importance of avoiding singlet exciton decay mecahanisms.

Electron and Hole Transport Layers

Adachi and co-workers[21] have extended the above idea to make a three layer structure in which the EL layer is sandwiched between an electron transport layer (ETL) and an HTL. The benefit of this is that it allows separate optimisation of the inorganic/organic injection interfaces, so that an organic with relatively high electron affinity can be chosen as the ETL material, and one with a low work function as the HTL material. The EL layer can then be chosen simply for a high Φ_F value, provided that electron transfer occurs smoothly at the heterojunction and that there are no deactivating processes such as exciplex formation. A later patent application[22] gives a detailed discussion of the consquences of different energy levels and band structures in devices of this type.

The first devices had very low Φ_{EL} values ($\approx$ 0.0001), but this was later improved[23] to about 0.05% with a half life of 5 hours. Subsequent papers from this group have extended the range of materials examined, described further increases in efficiency and discussed in more detail the key factors involved[24].

ELECTROLUMINESCENCE IN POLYMER FILMS

The use of polymeric films as EL devices was recently described by Friend *et al*[25], who described the use of poly(phenylenevinylene) (Figure 6a) to give red light emission. This discovery represents a potentially important new area for organic EL, and has prompted further work. Heeger et al[26] confirmed the result and reported improvements in Φ_{EL} to give up to 0.01%, and proposed a mechanism involving the neutral bipolaron exciton as an intermediate state. Further work by Friend and co-workers[27] questions the relevance of the bipolaron model and suggests that a simple singlet exciton may be involved. Polymers have also been used as the HTL, for example poly(vinylcarbazole)[28] or poly(methylphenylsilane)[29], which gave devices with a half life of a few seconds. EL was observed from the polysilane layer when a europium complex was added as a fluorescent dopant[30].

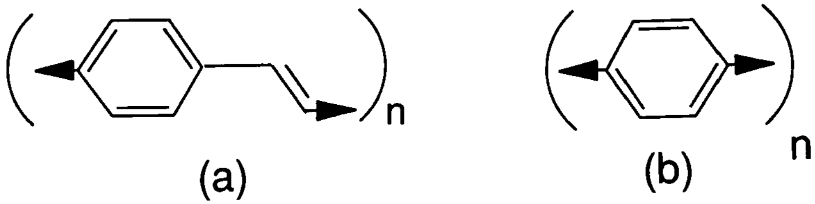


FIGURE 6 (a) Poly(phenylenevinylene), and (b) poly(phenylene).

Blue EL has recently been observed from poly(paraphenylene) (Figure 6b) films[31] with a Φ_{EL} of up to 0.05% at an operating voltage of 12V, and it is clear that a range of colours will become available from appropriate conjugated polymers. It is also clear that the use of polymer films does not provide any magic answers to the key issues of efficiency and lifetime.

CONCLUSIONS

Organic materials can give electroluminescence in a wide variety of colours, but at present the efficiency of devices is poor, and the lifetimes are too short to be practical for most applications. The challenge for workers in the field is to improve performance in these two key areas.

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