

an applied electric field when it is sandwiched between indium–tin oxide (ITO) and aluminum. Initially, the light emitted was very faint—yet it was bright enough to point to a new promising application for conducting polymers. Very soon afterward, visible red light emission was reported by Braun and Heeger using a poly(2,5-dialkoxy phenylene vinylene) as the emissive layer [10]. Following these two pioneering works, ever-increasing numbers of reports of electroluminescence in conjugated polymers have been published by scores of research groups from all over the world.

Conjugated polymers used for applications requiring good electrical conductivity usually need to be “doped” with strong acids or oxidants, which can lead to long-term stability problems even on storage. In contrast, an electroluminescent (EL) polymer needs only a low intrinsic conductivity, although the electric field strengths are so high that current densities can be quite appreciable. These EL polymers can be deposited from solution by simple spin-coating or dip-coating techniques over larger areas than are feasible by sublimed film techniques. Semiconducting polymers also usually have excellent thermal stability and good mechanical properties. These characteristics, in combination with control of color by the use of chemical design, make these materials serious competitors to existing light-emitting devices (LEDs) and flat panel technology.

Research into light-emitting polymers is still very new and is in its developing stage. Nevertheless, striking progress has been achieved over the past 7 years in many aspects; in improving processibility, in the tuning of color and color purity, in increasing device efficiencies and brightness, and in the construction of complicated device architecture. As a result, there are several companies with products now close to commercialization.

In this chapter, we will present the most recent state-of-the-art developments in this field as well as the basic principles behind the technology. Major issues discussed will include the following: (i) construction and operating principles of polymeric light-emitting devices (PLEDs); (ii) structures and synthetic strategies for light-emitting polymers; (iii) the control of the band gap and the tuning of color emission; (iv) improvement of device quantum efficiency; (v) multilayered PLEDs and charge-transporting polymers; (vi) potential applications of PLEDs.

II. CONSTRUCTION AND OPERATING PRINCIPLES OF PLEDs

A. Various Designs of PLEDs

Electroluminescence is the term used to describe the overall process that occurs when light is emitted upon application of an electric field to a semiconducting material. In inorganic materials, both alternating bias (AC) and direct bias (DC) modes are common. In organic devices, the major emphasis has been on DC applications for reasons explained later. The most common device architecture employed is shown in Figure 1. A fluorescent polymer is sandwiched between two metallic or conductive electrodes. At least one of these metallic contacts must be semitransparent for the light to escape normal to the plane to the device. The most widely used transparent conductor is indium–tin oxide (ITO), which is usually bought precoated on glass. On top of the ITO, an emissive polymer layer is coated directly from solution to a thickness of about 20–200 nm. To avoid shortcut circuits

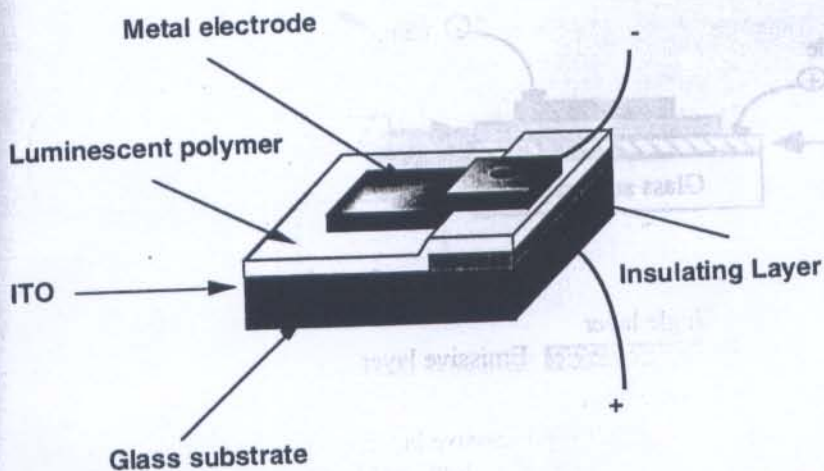


FIGURE 1 Schematic diagram of a typical single-layer-polymer-based LED.

between the positive and negative contacts through the extremely thin polymer layer, the ITO electrode is often patterned by etching, or an insulating layer can be used, as shown in Fig. 1. A charge-injecting metal contact such as calcium or aluminum is then typically deposited by vacuum evaporation. This simple, single-layer device can be constructed in a matter of hours in a standard laboratory and is expected to form the basis of a profitable new flat-panel industry.

To improve stability and to enhance device efficiency (photons of light emitted per injected charge), a multilayered device is usually employed. This involves the use of various electron and/or hole (positive charge carrier) transporting materials (Fig. 2). The use of one or two charge transporting layers is used to balance the injection of positive and negative charges into the emissive polymer, which leads to enhanced light emission. Detailed discussion on the use of charge transporting materials will be found in Section VI.

Whereas rigid, flat-screen devices are probably the most important application for emissive materials, the special properties of polymers allow for many other interesting applications. Polymers can be deposited by a number of techniques over a variety of large flat and curved surfaces, including spin-coating, dip-coating, electropolymerization, draw-coating, and spray-coating. With the likely exception of the last technique, all the others have been used to construct PLEDs. The pliable nature of most polymers also offers new possibilities to fabricate totally flexible LEDs. Gustafsson et al. realized a fully polymer LED [11] by using poly(ethylene terephthalate) as the substrate (Fig. 3), soluble polyaniline (doped with camphor sulfonic acid) as the hole-injecting and conducting electrode ($\sim 0.5 \mu\text{m}$), a red fluorescent PPV derivative as the electroluminescent layer (100–150 nm), and calcium ($< 100 \text{ nm}$) as the electron-injecting top contact. This PLED was found to be mechanically robust and could be sharply bent without failure. In addition, it shows high efficiency and a low turn-on voltage ($2\text{--}3 \text{ V}$).

Similarly, a kind of reversed cylindrical PLED can also be constructed. Figure 4 shows the structure used, in which a simple aluminum rod is used as the electron-

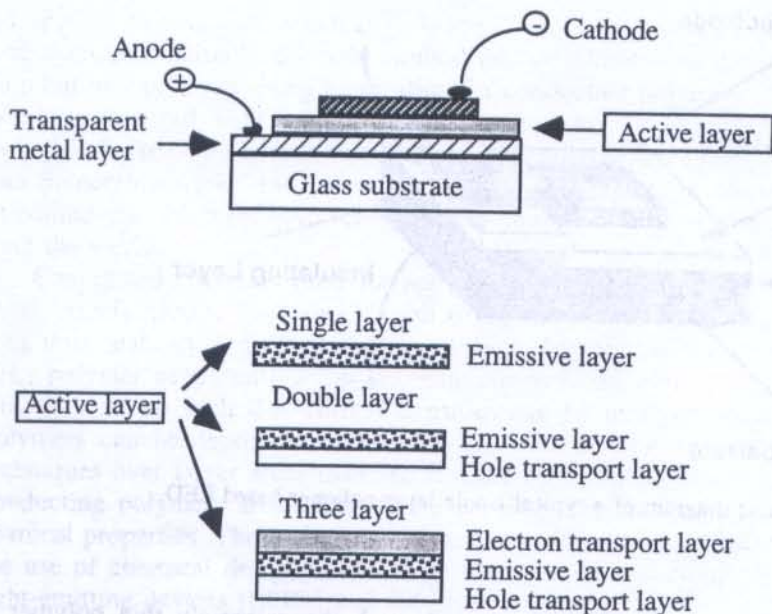


FIGURE 2 Cross-sectional view of a multilayered LED.

injecting substrate. Emissive polymer and hole-injecting polyaniline are subsequently deposited by dip-coating. Light emission was observed when the aluminum rod was biased negatively with respect to the polyaniline layer.

Discovered by Pei et al. [12,13], an unusual device configuration is the use of an electroluminescent polymer blended with an ionic conductive polymer. When this blend is sandwiched between two electrodes and sufficient potential is applied, a light-emitting *p-n* junction diode is created in situ through simultaneous *p*-type and *n*-type doping of the polymer on opposite sides of the device. Red, green, and blue light emission have been achieved by varying the electroluminescent polymer. The fabrication of this so-called light-emitting electrochemical cell (LEC) is principally the same as the above-mentioned PLEDs, but both the thickness of active layer and the nature of electrodes used are less critical than LEDs, due to the greatly

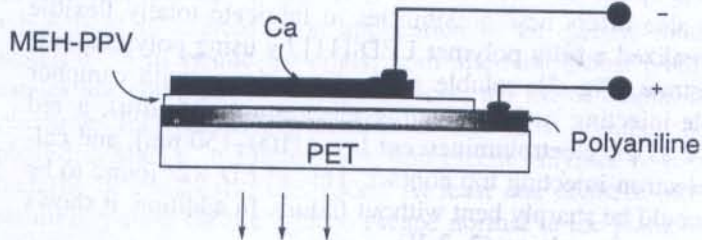


FIGURE 3 Cross-sectional view of the structure of a flexible PLED.

B. Basic Principles

Although PLEDs can be constructed in a wide variety of ways, the basic operating mechanism is the same in all cases. In order to understand the principles behind light emission in PLEDs, it is instructive to start with the simpler process of photoluminescence (PL) [18]. The great similarity between the EL and PL emission spectra of PPV [19] and other materials suggests that similar mechanisms are at play.

When a molecule is irradiated by light, photoexcitation of an electron from the highest occupied molecular orbital (HOMO) (or ground state S_0) to the lowest unoccupied molecular orbital (LUMO) generates an excited state (S_1) which can lose the absorbed energy in the following ways:

- (a) Radiationless transitions, such as internal conversion or intersystem crossing (macroscopically observable by heat formation)
- (b) Emission of radiation (fluorescence and phosphorescence)
- (c) Photochemical reactions (e.g., rearrangements, dissociations, dimerizations, photo-additions, reactions with neighboring particles, etc.).

Process (a) and (b) are represented schematically in Fig. 6.

Therefore, much of the light energy absorbed by a molecule may be lost by processes other than fluorescence. Indeed, it is rare for an organic compound to emit all of its absorbed energy back as light (i.e., to have a quantum efficiency of unity). As shown in Fig. 6, in most organic molecules the emitted light ($h\nu$) is of

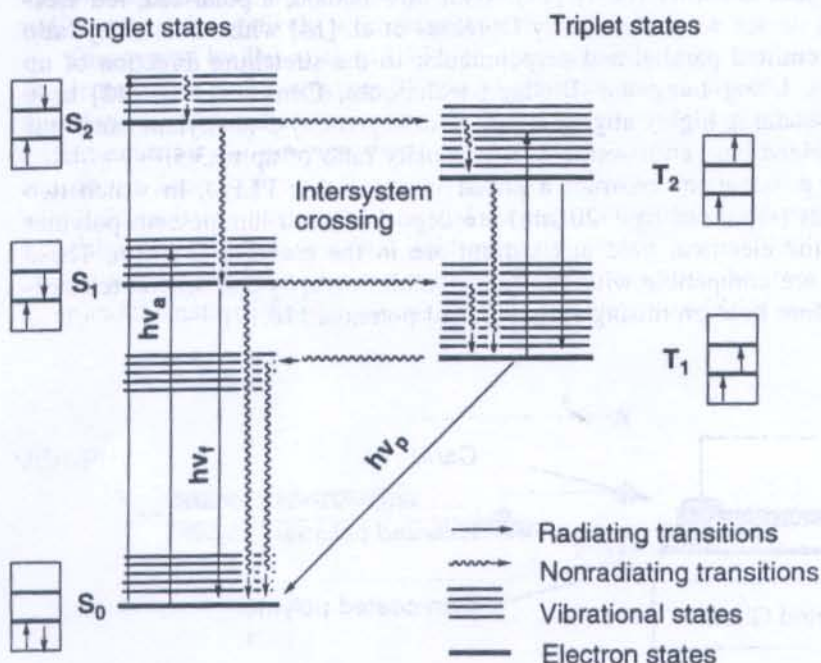


FIGURE 6 Relationship between absorption, emission, and nonradiative vibrational processes (Jablonski scheme).

a lower energy than of that originally absorbed ($h\nu_a$). This difference between absorbed and emitted light is termed the Stokes shift. Phosphorescence ($h\nu_p$) is usually very inefficient for organic materials at room temperature, and thus intersystem crossing does not lead to useful levels of light emission.

A simplified band scheme for the photoluminescence of a conjugated polymer system is shown in Fig. 7. Excitation of an electron from the polymers HOMO (or valence band) into the LUMO (or conduction band) is followed by a relaxation process to give an excited state known as a singlet exciton. This relaxation process, which involves both spatial reorganization of the conjugated backbone and a shift of the conjugated electrons, also results in a large Stokes shift. Nonradiative decay processes are not shown; for example, those involving the formation of charged species or the formation of triplet excitons (detected by photo-induced absorption) [20] which have been found to be the main channels to diminish emission efficiency in conjugated PPV.

The similarity between the PL and EL spectra in luminescent materials suggests that the same emitting species (a singlet exciton) is involved in each case. However, the mechanism of formation is much more complicated in the latter case. Injection of electrons into the LUMO of the polymer can occur at one electrode and removal of electrons from the HOMO can occur at the other [the process of removal of a negative charge from the HOMO leaves a positive charge (or hole) in the band]—this process is more usually referred to as hole injection. Under the influence of the applied electric field, the oppositely charged species tend to drift toward each other. The combination of the charge carriers occurs on a segment of polymer chain to form a singlet exciton, which can then radiatively decay with the emission of visible light.

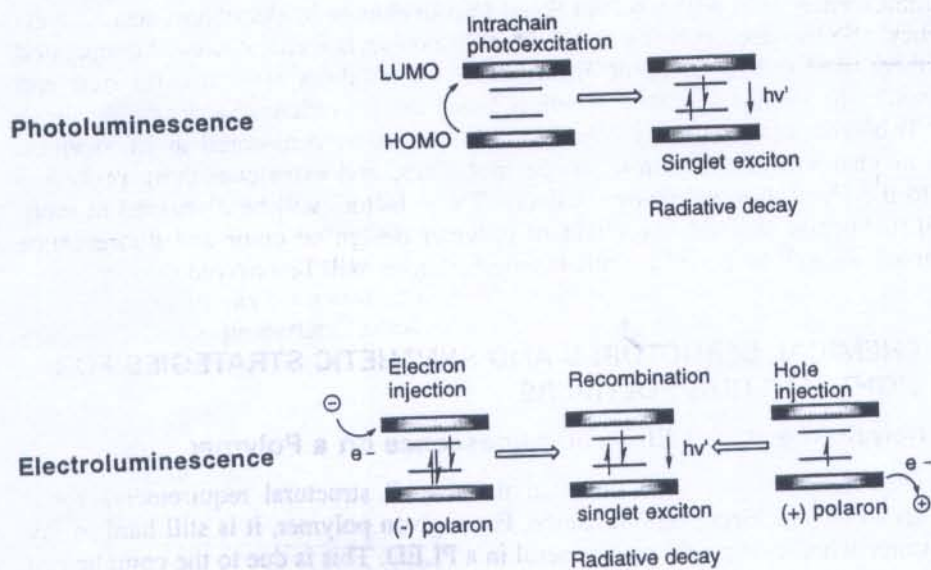


FIGURE 7 Comparison between photoluminescence and electroluminescence in conjugated polymers. (Adapted from Ref. 18.)

Emission spectra from polymeric LEDs are generally very broad due to vibronic side bands and the inhomogeneity of the material (defects, kinks in the structure, etc.). This can be partially overcome by the use of Fabry-Perot microcavity structures. Striking modifications to both EL and PL emission involving narrowing/strengthening of the main transition have been achieved [21,22].

Photoluminescent efficiencies are usually defined simply as $(\text{photons emitted} / \text{photons absorbed}) \times 100\%$. However, there is a wide range of ways that can be used to define EL efficiencies. One of the most common is device quantum efficiency, defined as the ratio of photons emitted/charge injected (both holes and electrons) $\times 100\%$. Much of the light (up to 75%) of any light generated within a simple LED can be lost through absorption and wave-guiding out the edges instead of going in the useful forward direction. Thus, a further distinction must be made between external quantum efficiency, which measures the light leaving the device, and internal quantum efficiency, which is based on the calculated total amount of light generated within the film. Device brightness is often reported in the units of candela per meter squared. A figure of 100 cd/m^2 is considered bright enough for a flat panel display, whereas for lighting applications up to 5000 cd/m^2 may be required. The best organic devices can often achieve the latter figure (up to $90,000 \text{ cd/m}^2$ has been reported [23]), although not necessarily for prolonged periods.

Internal efficiency measurements can be very useful as, in principle, they give information on how much further a device can be improved. Unless otherwise stated, efficiencies quoted in this chapter should be taken to be internal. As nonemitting triplet states are also generated when two charge carriers combine to form an exciton, the maximum internal efficiency possible is believed to be 25%, although this figure has been challenged as possibly being too high by some workers, as well as being too low by others.

The close relationship between the PL and EL implies that increasing the photoluminescence yield will result in equal improvements in electroluminescence efficiency, all other factors being equal. Photoluminescence efficiencies of conjugated polymers used in PLEDs range from below 1% to about 80% in solid state and can reach almost up to 100% in solution. However, EL efficiencies are rarely above 5%. This indicates that many other factors have to be considered in EL devices, such as charge-injection ratios, charge mobilities, and extra quenching processes due to the electrodes and charge carriers. These factors will be discussed in more detail in Section V. First, the effect of polymer design on color and fluorescence efficiency as well as general synthetic methodology will be covered.

III. CHEMICAL STRUCTURES AND SYNTHETIC STRATEGIES FOR LIGHT-EMITTING POLYMERS

A. Requirements for Electroluminescence on a Polymer

Very little research has been done on the overall structural requirements for a polymer to exhibit electroluminescence. For a given polymer, it is still hard to say in advance whether it would prove useful in a PLED. This is due to the complicated mechanism for singlet exciton formation in these devices, which involves double charge injection, charge transportation, recombination, and emission. It is quite common for a given material to give poor results with one electrode or charge

transport material, but excellent performance with others. The most important prerequisite for the emissive layer is that polymer must be fluorescent.

Several electronic considerations are believed to be important in order to favor photoluminescence in organic compounds. In photoluminescent compounds generally, the longest wavelength of absorption corresponds to a $\pi \rightarrow \pi^*$ excitation. On the other hand, species in which the longest absorption wavelength corresponds to an $n \rightarrow \pi^*$ transition (common in molecules containing heteroatoms or heterocyclic aromatic molecules) are seldom fluorescent [24]. Thus, it is not strange that both polypyrrole and polyaniline are not fluorescent, although they are good semiconducting polymers. It is observed that the excited singlet state normally has a half-life of about 10^{-8} s. If the half-life is more than 10^{-8} s, intersystem crossing will be favored; a shorter half-life implies rapid deactivation of the molecule by other processes.

The fluorescence behavior of an organic compound is dependent on three main factors, namely the nature of the carbon skeleton, the geometrical arrangement of the molecule, and the type and position of any substituents. Increasing the extent of conjugation and therefore increasing the mobility of the π electrons often results in an increase in fluorescence intensity. For instance, anthracene has a higher efficiency (0.32 in hexane) than naphthalene (0.1 in hexane), which, in turn, is more fluorescent than benzene (0.04). Increasing planarity and rigidity also helps to increase fluorescence, as both will also enhance the free mobility of the π electrons and charge transportation. In solution, increased rigidity can also help by reducing vibrational-rotational interactions in the excited state, which can lead to intersystem crossing. Biphenyl and fluorene possess the same degree of conjugation, but the aromatic rings in the latter compound are held rigidly in a planar configuration, whereas those in biphenyl are not. Fluorene (Fig. 8) has a quantum efficiency of about 0.54 in hexane, whereas that of biphenyl is only 0.23 [25].

However, if the extent of conjugation is very large, other effects can come into play. The mobility of excited states tends to increase as the conjugation increases, thus they are more likely to encounter a quenching centre before decaying radiatively, and so reduce emission intensity. As well, the band gap can decrease to an extent (< 1.5 eV) where thermal deactivation of excited states can become important. Time-resolved photoluminescence of poly(*p*-phenylene vinylene) in the picosecond regime shows [26] that the nonradiative decay rate increases with increasing polymer chain conjugation length and that the luminescence decay is much faster for excitation parallel to the polymer chain than for perpendicular excitation.

The substituents on a conjugated system may have a very profound effect on the fluorescence properties. Substituents which enhance π electron mobility will

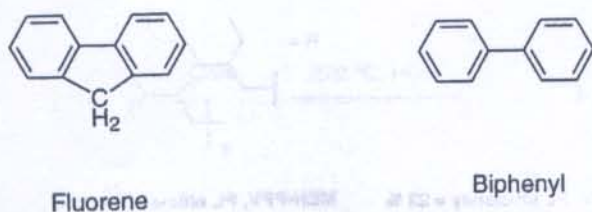


FIGURE 8 The structural comparison between fluorene and biphenyl.

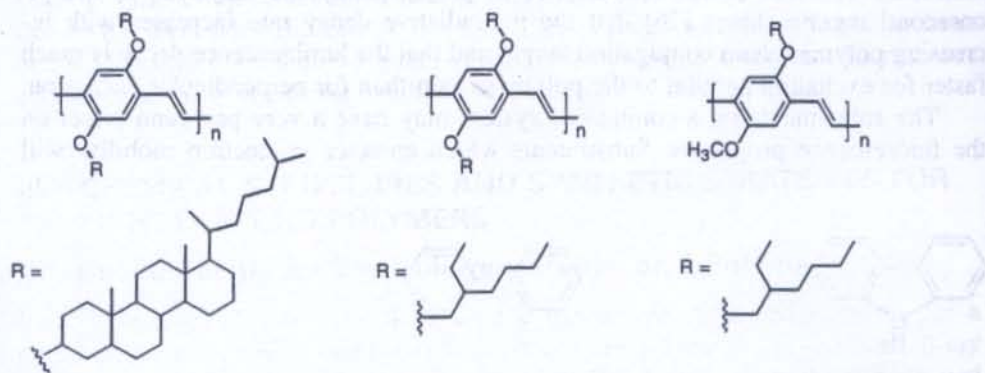
normally increase fluorescence. Often, a combination of electron-donating (positively mesomeric) substituents, such as $-\text{NH}_2$, $-\text{N}(\text{CH}_3)_2$, OCH_3 , and OH , with electron-withdrawing substituents, such as $\text{C}=\text{O}$, CN , SO_3H , and COOH , is used to enhance fluorescence. Alkyl groups generally have little effect on fluorescence except on steric grounds. Large atoms such as bromine and iodine will reduce fluorescence wherever they occur as substituents, due to enhancement of intersystem crossing.

Photoluminescence can often be greatly enhanced by increasing the intrinsic stiffness of a polymer backbone or by inducing large bulky side groups to weaken intermolecular interactions [27]. This is shown in Fig. 9, where the use of larger side groups in PPV derivatives lead to higher photoluminescent efficiencies. However, very large aliphatic side chains may cause problems in EL devices by lowering the overall charge carrier mobility.

The fluorescence-structure relationships of heterocyclic compounds are poorly understood at present. However, it appears that heterocyclics with a longest absorption wavelength corresponding to an $n \rightarrow \pi^*$ transition are likely to be nonfluorescent, whereas those corresponding to a $\pi \rightarrow \pi^*$ transition are more likely to be fluorescent. For instance, pyridine is nonfluorescent, whereas quinoline is weakly fluorescent. However, both polypyridine and polyquinoline are much more fluorescent as the $\pi \rightarrow \pi^*$ transition becomes more dominant.

B. Synthetic Strategies for Light-Emitting Polymers

One of the main problem with highly conjugated polymers is their lack of processibility, as most of them are neither fusible nor soluble due to their rigid backbones and strong intermolecular interactions. In order to get around this problem, several synthetic strategies have been developed during last several years. These include (a) soluble precursor routes, (b) conjugated polymers with long flexible solubilizing groups, and (c) copolymers containing fixed conjugated segments and flexible or angular spacers.

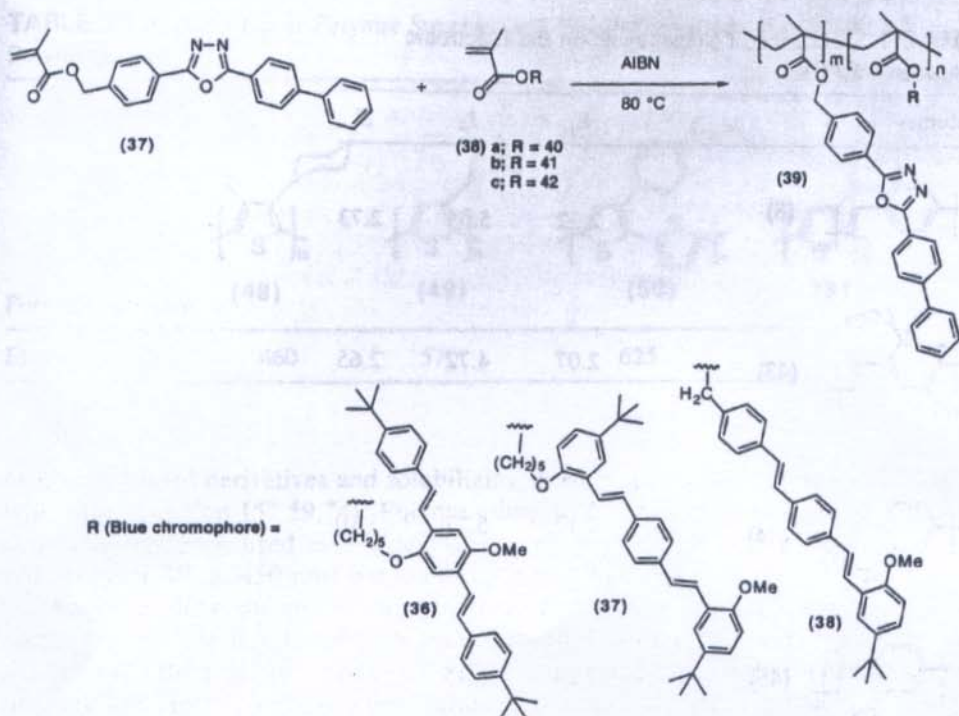


BCHA-PPV, PL efficiency = 66 %

BEH-PPV, PL efficiency = 22 %

MEH-PPV, PL efficiency = 20%

FIGURE 9 The influence of side-chain structures on PL efficiency in PPV derivatives.



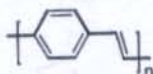
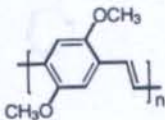
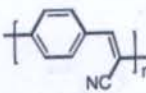
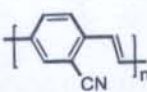
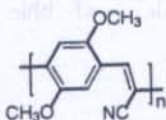
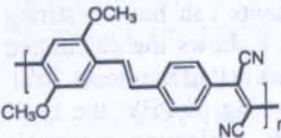
SCHEME 11 Synthesis of PMMA bearing with aromatic oxadiazoles and blue chromophores.

There are several approaches that can be used to vary the band gap and emission of a conjugated polymer. The nature of any substituents can have a strong influence, either through electronic or steric effects. Table 1 shows the calculated variation of electronic properties of several PPVs with various substituents [69]. For instance, by using alkoxy substitution on the benzene ring of PPV, the band gap (E_g) can be reduced significantly, leading to red LEPS. Ionization potentials can be tuned by the inclusion of electron-donating groups such as alkoxy or amino substituents, or the presence of electron-withdrawing substituents such as the cyano group.

The band gap of many thiophene-based polymers can be tuned by changing the size of the substituents. In polythiophenes, enhanced steric hindrance from side groups leads to increasing planarity of the main chain and an increasing band gap. A range of thiophene-based polymers have been synthesized with emissive colors spanning the entire visible spectrum and beyond (Table 2) [70].

Another way of blue-shifting the emission of conjugated polymers is to incorporate conjugation-breaking units in the main chain. This can be achieved by deliberate incorporation of nonconjugated comonomers, or by controlling the polymerization or postpolymerization conversion conditions [71]. Various conjugation-breaking linkages may be used, including flexible alkyl or alkoxy spacers, meta-benzene, and the elements O, S, N, and Si. Limiting the conjugation

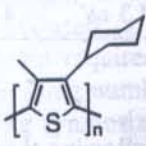
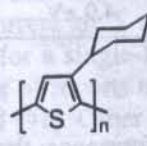
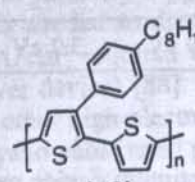
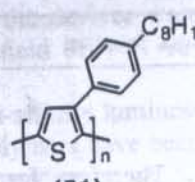
TABLE 1 Influence of Substituents on the Electronic Properties of PPVs

Polymer	E_g	I_p	E_a
 (6)	2.32	5.05	2.73
 (43)	2.07	4.72	2.65
 (44)	2.17	5.27	3.10
 (45)	2.24	5.15	2.91
 (46)	1.97 1.57	5.12	3.15
 (47)	1.74	5.06	3.24

Note: I_p = ionization potential; E_a = electron affinity; E_g = band gap.

of a polymer in such a way often has a useful effect of increasing the fluorescent efficiency, in part due to lowering exciton diffusion rates. This was achieved in a PPV precursor polymer by limiting the degree of final conversion into the fully conjugated polymer [72]. In another example, incorporation of a small amount of a comonomer into a normal PPV-sulfonium precursor polymer results on conjugation-breaking segments and improved EL efficiency [73]. However, this resulted in a statistical incorporation of a comonomer, and, hence, a wide range of conjugation lengths was produced. For more effective control of color, one can use a nonconjugated polymer containing small chromophores either in the main chain or the side chain. As an example, several block copolymers containing distyrylbenzene

TABLE 2 Relationship of Polymer Structure and Electroluminescence Emission of Polythiophenes

Polymer structure				
	(48)	(49)	(50)	(51)
EL peak (nm)	460	570	625	685

or its substituted derivatives and solubilizing flexible spacers have been synthesized with blue emission [57,59,74]. Polyquinoline with a hexafluoropropylene linkage or spacer has been used as a blue PLED with high efficiency (internal quantum efficiency of 4% at 450 nm) but low brightness (30 cd/m²) [75].

Polyphenylene and its derivatives represent a typical blue-light-emitting polymer, although the exact emission may vary from violet to green depending on substituents. Because the first blue PLED was reported using poly(*p*-phenylene) as the emissive layer [76,77], a whole series of soluble blue-light-emitting PPPs have been synthesized [15,46,78–81]. The phenylene units can be bridged to form “ladder”-type PPPs, with the aim of obtaining more stable and efficient blue emission [82,83]. Device efficiencies as high as 4% have been achieved using these materials [84].

Microcavity structures have received a great deal of attention for their ability to tailor the emission properties of LEDs. In particular, the broad-emission characteristics of most organic materials can be transformed into a very narrow output spectrum [21]. By using such a structure, lasing pumped optically in a high-*Q* cavity has been recently demonstrated [85,86].

V. IMPROVEMENT OF DEVICE QUANTUM EFFICIENCY

Initial reports of conjugated polymer electroluminescence involved poly(phenylene vinylene) derivatives, with device quantum efficiencies of only 0.01–0.05% [9]. Soon after, up to 1% quantum efficiency was achieved using a PPV copolymer containing nonconjugated segments [87]. The most striking improvement of quantum efficiency is perhaps a double-layer red PLED using a cyano-substituted PPV as the emissive layer and PPV as the hole transport layer with a 4% internal quantum yield (as detailed below) [88]. Efficiencies of close to 11% have been achieved in another cyano-PPV derivative [82], which given the PL efficiency of the polymer of ~40%, may be close to the maximum theoretically possible.

The quantum efficiency in PLEDs is affected not only by the nature of the emissive polymer but also by the device structure. This is because other important aspects include charge carrier transport to and within the material and unwanted exciton quenching reactions—especially at the metal electrode interfaces.

TABLE 3 Work Function of Several Metals

Metal	Ca	Mg	ITO	Al	In	Ag
Work function	2.9 eV	3.7 eV	4.9 eV	4.3 eV	4.2 eV	4.4 eV

Therefore, for optimum device performance, the following three factors should be considered: (1) carrier injection and transport; (2) formation of excitons; and (3) radiative recombination of excitons [89]. This can be written as

$$\phi_{ei} = \phi_{pl}\phi_i\phi_e$$

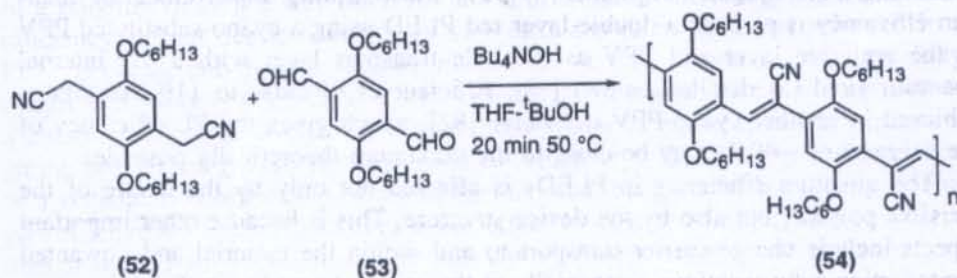
where ϕ_{pl} is the photoluminescence efficiency, ϕ_i is the charge balance efficiency, and ϕ_e is the singlet exciton quantum yield (often taken to be 25%).

Thus, it is very important to equalize the number of electrons and holes reaching the emissive zone to maximize ϕ_i . PPV is a widely used material in PLEDs but has a low oxidation potential, as do many other simple conjugated polymers. Under normal circumstances, mainly holes are injected into the polymer, leading to poor EL efficiencies. It is therefore necessary to enhance electron injection into many such polymers.

The most direct method is to use a low work-function metal to improve electron injection. Many luminescent polymers show much higher EL efficiencies when calcium is used as the electron-injecting contact as compared to most other metals. Unfortunately, calcium is well known to oxidize very easily when in contact with air or moisture, and, hence, may not be useful in a commercial environment. Table 3 lists some common metals and their work functions. Often, mixtures of metals are used to give a combination of low work function and increased environmental stability, such as Mg/Ag and Li/Al alloys.

Another way is through the use of polymers with a much higher electron affinity. This has been achieved by the Cambridge group by synthesizing a PPV-derivative (54) with electron-stabilizing cyano-substituents [90]; see Scheme 12.

This red polymer has an optical energy-gap of 2.05 eV (as measured by the onset of absorbance), which is very close to MEH-PPV but with a much higher PL efficiency. A single-layer device both using aluminum and calcium gave devices with 0.15% efficiency. Furthermore, the improved electron affinity also allowed the



SCHEME 12 Synthesis of cyano-substituted PPV.

use of the more stable aluminum metal as cathode without a loss of efficiency. Remarkably, an internal efficiency of 4% was found with a double-layer device (ITO/PPV/CN-PPV/Al). Its emission proved to be solely from the cyano polymer with a peak wavelength of 710 nm. The fields needed to drive the devices were also significantly reduced (a current of 5 mA/cm² required a field of 4×10^5 V/cm, about half that required for a single-layer device) [88].

There are increasing number of reports of other high-electron-affinity luminescent polymers being synthesized [91]. Other cyano-substituted polymers have been reported [90] and heterocyclic electron-deficient rings (such as pyridine or oxadiazole) have also been used.

Alternatively, electron injection can also be improved through the use of an extra electron-transporting layer. Examples include high-band-gap materials such as oxadiazoles or triazines that also have a high oxidation potential. Thus, they often function by blocking hole transport, rather than necessarily having a high natural electron affinity. (2-(4-Biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole) (PBD) is a very commonly used compound in such layers [92,93]. More details about charge-transporting polymers will be discussed in the next section.

A prime consideration when improving efficiencies is to enhance the fluorescence quantum yields of the materials involved. This can often be achieved through elimination of defects or impurities, or prevention of crystallization. However, many stable and potentially attractive materials such as perylene derivatives show poor fluorescence in the solid state, but high fluorescence in dilute solution. Thus, by blending different polymers to form solid-state solutions, often much higher PL and EL efficiencies are possible than by using either material alone. General considerations for improving PL are discussed in previous sections. However, it is not uncommon for EL efficiency to decrease with increasing PL efficiency due to other factors [42].

In electroluminescence, the existence of a bound triplet excited state can severely limit the quantum efficiency. If the triplet binding energy and the corresponding cross section for forming a triplet from a pair of injected carriers were large, the singlet to triplet ratio would be determined by spin statistics (3:1). That means the maximum EL quantum efficiency would be limited to 25%. Although this limitation has been generally accepted, Pakbaz et al. [94] pointed out that if the dynamics are such that the cross section for triplet formation from a pair of oppositely charged free carriers is relatively small, the limiting quantum efficiency could approach 100%. This is very encouraging, but the state of art is still far from even 25%.

VI. CHARGE TRANSPORT POLYMERS AND MULTILAYERS PLEDs

As mentioned above, electron injection and transport is often much more difficult than it is for holes. It is very common to use electron-transporting layers to try to equalize the two kinds of charge injection and transportation. In one of the first examples in PLEDs, Burn et al. [87] reported a 10-fold enhancement of internal efficiency by using (2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole) (PBD)/poly(methyl methacrylate) (PMMA) blend on top of PPV. It was considered that the role of the electron transport layer is to confine holes to the emissive layer, as shown in Figure 11.

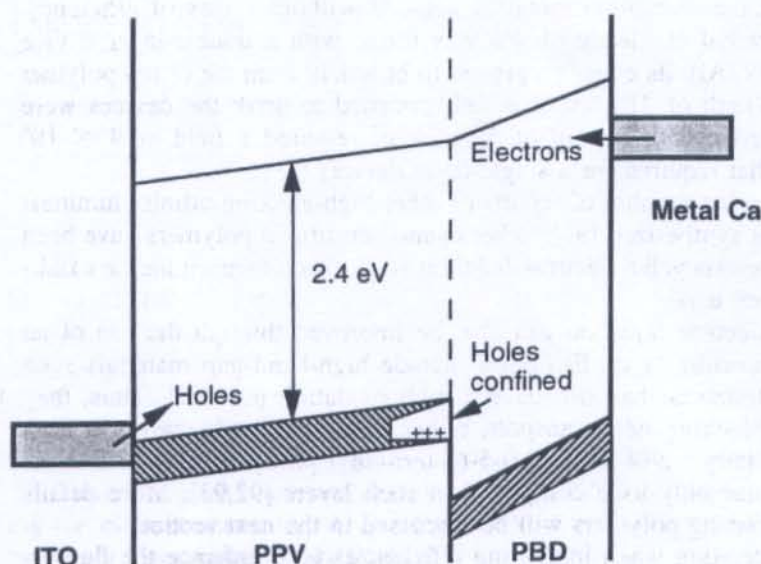


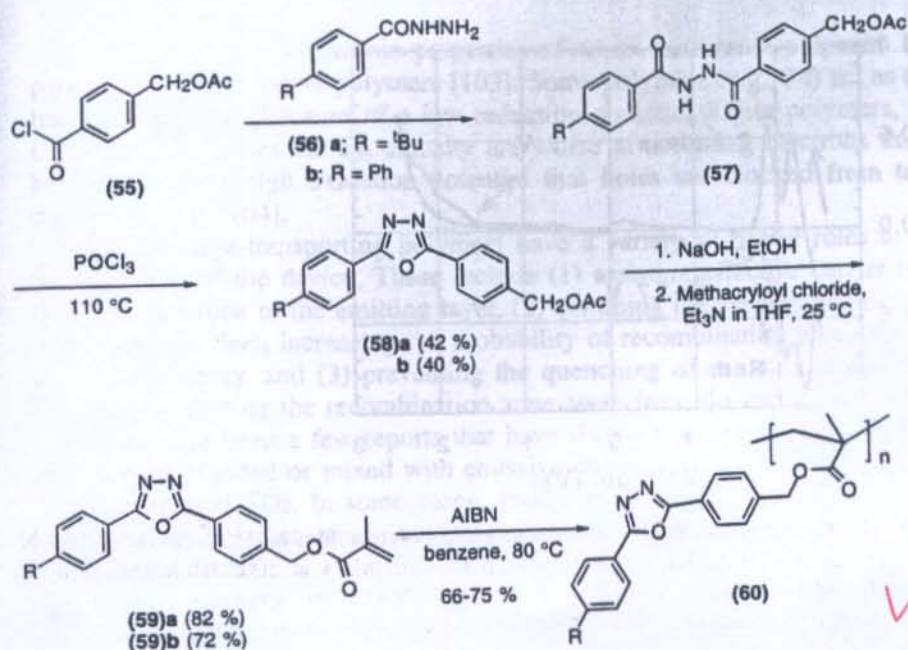
FIGURE 11 Schematic band diagram of a double-layer device under a forward bias utilizing PBD/PMMA as electron-transporting/hole-blocking layer.

A polymer blend with PMMA was used in this case, as good quality PBD films cannot be cast directly from solution due to crystallization. Although such polymer-dispersed films have enjoyed wide application in multilayered PLEDs, such devices tend to suffer from short lifetimes. It is believed that this may be due to problems such as aggregation and recrystallization of the PBD under operation. To address this issue, many polymers containing PBD or other electron-deficient aromatic heterocycles have been synthesized. In a typical example, Li et al. [63] reported a polymethacrylate bearing aromatic oxadiazoles side chains; see Scheme 13.

These polymers were used in various multilayered devices with PPV as the emissive layer. Compared with single-layer PPV devices, the internal efficiency of the two-layer PPV device with oxadiazole-bonded PMMA (60) as the charge-transporting layer was increased by a factor of 4 to 0.04% (at a current density of 0.5 mA/cm²). It was also observed that the turn-on voltage for the two-layer device was significantly lower than that of an analogous single-layer PPV device, as shown in Fig. 12. The downturn in efficiency shown in the inset of Fig. 12 on increased current may be due to a number of effects, such as heating or charge-carrier-induced quenching.

A similar polymethacrylate-PPD derivative and several polyethers containing PPD units have also been reported by Bell AT&T laboratories [95]. LEDs containing these electron-transporting (ET) polymers were found to be much more stable than those without an ET layer. However, increased efficiencies were not always found with these EL layers [96].

Processable main-chain oxadiazole polymers have also been synthesized via incorporation of flexible spacers [97–99], or by a precursor route [100]. Oxadiazole-containing polymers are usually wide-band-gap materials and are,



SCHEME 13 Synthesis of polymethacrylate polymers bearing PPD and PBD.

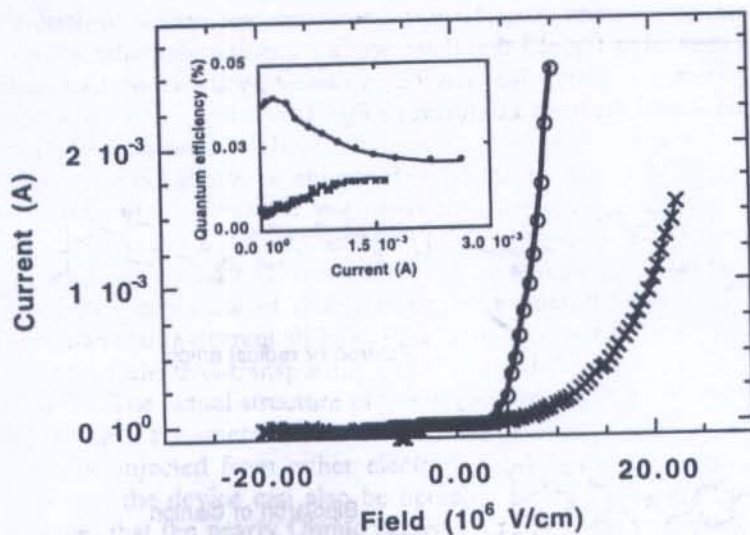


FIGURE 12 Comparison of LED characteristics by using PMA-PPD as electron transporting (\times : ITO/PPV/Ca; \circ : ITO/PPV/PMA-PPD/Ca).

Table 4 lists the electronic properties of some oxadiazole polymers in comparison to some emissive polymers [103]. Some polymers (e.g., 54) act as electron transport materials because of a low reduction potential. Other polymers, such as the oxadiazole series 62–64, actually are worse at accepting electrons than PPV, but have such a high oxidation potential that holes are blocked from traveling through [63,101,104].

These charge-transporting polymers have a variety of useful roles to play in the operation of the device. These include (1) assisting effective carrier injection from the electrode to the emitting layer, (2) confining the carriers within the emitting layer and, thus, increasing the probability of recombination processes leading to radiative decay, and (3) preventing the quenching of excitons at the electrode interface by shifting the recombination zone away from the metal.

There have been a few reports that have shown that charge-transporting polymers can be blended or mixed with emissive polymers or compounds to construct single-layered PLEDs. In some cases, good results were obtained upon mixing a hole transport polymer, an emissive material, and an electron-transporting material into a single blend.

Because aromatic oxadiazole polymers show good photoluminescence as well, light emission from these charge-transporting polymers has also been demonstrated if a good hole-transporting layer, such as polyaniline, was used. Berggren et al. obtained white light emission [105] and violet emission [106], respectively, by blending geometrically restricted polythiophenes with an oxadiazole compound (PBD), which played both a charge-transporting and electroluminescent role.

In some cases, the use of hole transport polymers can also improve the PLEDs performance. This is especially effective when emissive polymers with higher electron affinity are employed. For instance, the efficiency of double-layer devices (ITO/PPV/CN-PPV/Al) exhibit a 20-fold increase in efficiency over single-layer cyano-PPV devices, the PPV layer acting solely as a hole-transporting material. Polyoxadiazole polymers show poor light-emitting performance in a single-layer device, whereas bright-blue light emission was achieved by incorporating a polyaniline hole transport layer [97]. By using electropolymerized poly(3-*n*-octylthiophene) as a hole-transporting layer, light emission from an organic chromophore could also be enhanced [107]. An increase of 100-fold in internal quantum efficiency was achieved by dispersing a nonconjugated blue-luminescent copolyester containing 1,2-dinaphthylene vinylene units, PBD (electron-transporting compound) and poly(9-vinylcarbazole) (hole-transporting polymer) [108].

By careful use of charge-transporting materials, Wang et al. have constructed an alternating-current PLED [109]. This device has more symmetry than is usual, with an electron-transporting material sandwiched between two hole-transporting layers. The actual structure of the device was Al/EB/PPy/EB/ITO-glass, in which EB stands for emeraldine base form of polyaniline and PPy for polypyridine. Holes can be injected from either electrode, and due to the relatively fast dynamic response, the device can also be operated in an alternating current mode. It is suggested that the nearly Ohmic behavior of the electrode-redox polymer contact and the presence of a large density of redox polymer-emissive polymer interface states have a central role in the operation of the device.