POLYMER LIGHT EMITTING MATERIALS AND DEVICES

by Ye Tao and Marie D'Iorio

In the past 10 years, conjugated polymeric materials have demonstrated clearly their potential for use in light emitting devices, thin film field effect transistors and photovoltaic cells. The low device fabrication cost, large device area, flexibility, and robust mechanical properties are among many advantages of applying polymeric materials in electronic and optoelectronic devices. In this article, we will discuss some basic electronic processes involved in the photon-excited light emission in conjugated polymeric materials, and the electroluminescent process in polymer light emitting devices as well as the factors affecting the device performance and efficiency. We will also review briefly the recent progress in the field of polymer light emitting materials and devices.

The low device fabrication cost, large device area, flexibility, and robust mechanical properties are among the many advantages of applying polymeric materials in electronic and optoelectronic devices.

INTRODUCTION

Conjugated organic materials have been known to exhibit strong photoluminescence and are thus potential materials for electroluminescence for telecommunication and information display applications. Although electroluminescence in inorganic materials had been known since 1936 with the pioneering work of Destriau [1] in ZnS phosphors, it was only in 1963, that Pope, Kallmann and Magnate [2] reported electroluminescence in organic materials: single crystals of anthracene. Schneider and co-workers at the National Research Council of Canada (NRC) performed some of the pioneering work in understanding electroluminescence in such materials [3,4]. Practical applications did not result from this early work because of the large driving voltages and the poor charge injection into the single crystals. The problem of the large driving voltage was eliminated by the use of thin film deposition techniques- Langmuir-Blodgett film deposition and vacuum sublimation of amorphous thin films of anthracene [5,6]. The efficiency of these devices was still very poor and it would take another decade of work before Tang, and Van Slyke [7] could fabricate low voltage (10V), bright organic light emitting devices from thin organic films of triarylamines and tris(8-hydroxyquinolato) aluminum (Alq$_3$). This breakthrough was followed shortly afterwards with the demonstration by Burroughes *et al.* of electroluminescence in conjugated polymer films based on poly(p-phenylenevinylene) (PPV). At about the same time, polymeric semiconductors which could be cast as thin films were developed; this led to the fabrication of organic field effect transistors based on conjugated polymers and oligomers (α-sexithienyl and pentacene) with field effect mobilities and current on-off ratio comparable to that of amorphous silicon at room temperature [8-11]. The last decade has seen a multidisciplinary thrust in designing stable, high performance organic and polymeric materials for flat panel display and plastic electronics applications and a concurrent effort in understanding the electronic and optical transport properties of such materials. For a wide range of modern applications including televisions and computer monitors, it would be useful to have inexpensive, efficient and lightweight flat panel displays. The flat panel display market is currently dominated by active-matrix liquid crystal displays that can provide high intensity color images at video rates. Weak points for this technology are high production costs for displays which are more than 8 cm across, a power hungry back light to operate in a dark environment, sluggish operation and narrow viewing angle. In order to compete with liquid crystal displays, any electroluminescent material must perform with a drive voltage of less than 5 V, have an operating lifetime (i.e. time needed for light emission to degrade to half the initial value at constant current) of more than 10,000 hours and operate in the temperature range of –30 to 80 °C, with an external quantum efficiency of 2-5% (0.02-0.05 photons/electron). In the last decade, a multidisciplinary effort has been underway to design, synthesize and test molecular and polymeric materials that meet these specifications for the eventual commercialization of organic light emitting diodes (OLEDs) and polymer light emitting diodes (PLEDs).

The first polymer LED demonstrated by the Cambridge group [12] emitted green-yellow electroluminescence by using poly(p-phenylenevinylene) (PPV) as a semiconductor layer in a single-layer (ITO/PPV/AL) device structure as illustrated in Figure 1. In this structure, the indium tin oxide (ITO) layer acts as a transparent anode, and allows the light generated in the diode to emit from the device. The layer of electroluminescent polymer is usually prepared using a solution spin-coating method. The electroluminescent material carries out the injection and transport of both electrons and holes as well as facilitates the radiative decay of excited molecular states to the ground state. The cathode is usually prepared by vacuum evaporation of low work function metals, such as Ca, Mg, Al or Mg:Ag and Al:Li alloys. During operation,

Ye Tao, Marie D'Iorio <Marie.D'Iorio@nrc-cnrc.gc.ca>, Institute for Microstructural Sciences, National Research Council of Canada, Montreal Road, Ottawa, ON, K1A 0R6

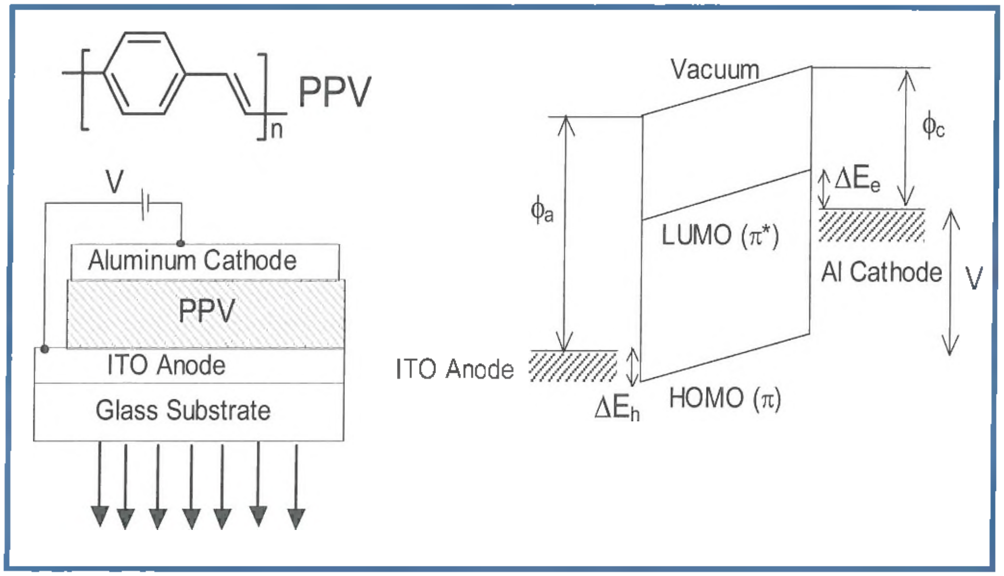

Fig 1 The first polymer LED demonstrated by the Cambridge group using as a semiconductor layer in a single-layer (ITO/PPV/AL) device structure.

electrons are injected from the low work function cathode into the π^*-band of the PPV and holes are injected from the ITO anode into the π-band. Under the influence of the electric field, the charge carriers move through the polymer layer over a certain distance until electrons and holes capture one another within the PPV layer, and form bound excitons. The radiative decay of the excitons produces light emission. Ideally, the work functions of the cathode (ϕ_c) and anode (ϕ_a) should be matched to the π^*-band and π-band, respectively. In reality, however, the match is imperfect producing different barrier heights for electron (ΔE_e) and hole (ΔE_h) injection that occur via a combination of Fowler-Nordheim tunnelling and thermionic emission. It is very clear from this picture that the operation of polymer light emitting diodes depends on the following three basic processes: 1) charge injection through the electrodes, 2) charge transport within the polymer layer, 3) recombination and radiative decay.

In the following, we will introduce some aspects of these fundamental processes in PLED operation, and briefly survey issues related to device structure design and fabrication as well as materials development for PLED application.

SOME FUNDAMENTAL PROCESSES IN CONJUGATED POLYMER DEVICES

Conductivity in Conjugated Polymers

Conjugated polymers are a novel class of materials that possess the optical and electronic properties of semiconductors with the processing advantages and flexible mechanical properties of plastics. Conjugated polymers are macromolecules (typically long molecular chains) with alternating single and double chemical bonds. Typical examples are polyacetylene, polyphenylene, and polyphenylene-vinylene (Figure 2).

Trans-polyacetylene is the simplest conjugated polymer system. In this structure, three of the four carbon valence electrons are in sp^2 hybridized orbitals: two of them are σ type bonds with neighbouring carbon atoms along the one-dimensional backbone. The third electron forms a bond to a hydrogen atom, while the fourth is in a $2p_z$ orbital and forms a π-bond. The σ-bonds form a low-lying, completely filled energy band, while the π-bonds form a partially filled band. If all the bonds were of equal length, i.e. the conjugated double bonds were completely delocalised, trans-polyacetylene would be a quasi-one-dimensional metal due to the half filled band.

However, this delocalised state is not stable [13] and the molecule performs a Peierls transition leading to an energetically lower state (Figure 3(a)). The double bonds are now alternating and the metallic conductive properties are lost in the so-called dimerized state. The localization of the double bonds also leads to an alternation of the distance between the carbon atoms since the double bonds have a slightly shorter bond length. This effect of the dimerization can be measured by x-ray diffraction, and the difference in length is found to be 0.03 Å [14].

There are however two possible configurations. Because of the symmetry of trans-polyacetylene, both configurations are equivalent and have the same energy. The ground state is therefore degenerate. The presence of two configurations of these conjugated polymers results in the possible formation of different domains (Figure 3(b)) along the polymer chain. The domain walls are structural defects that are found to have strong influence on the conductivity of these polymers. The situation is depicted in Figure 3(c) where a dangling bond appears where the two domains meet. This type of

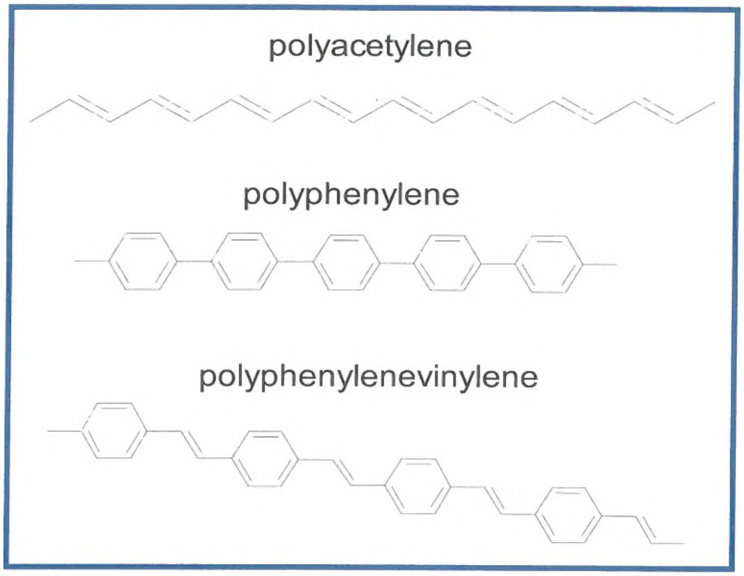

Fig 2 Some examples of conjugated polymers

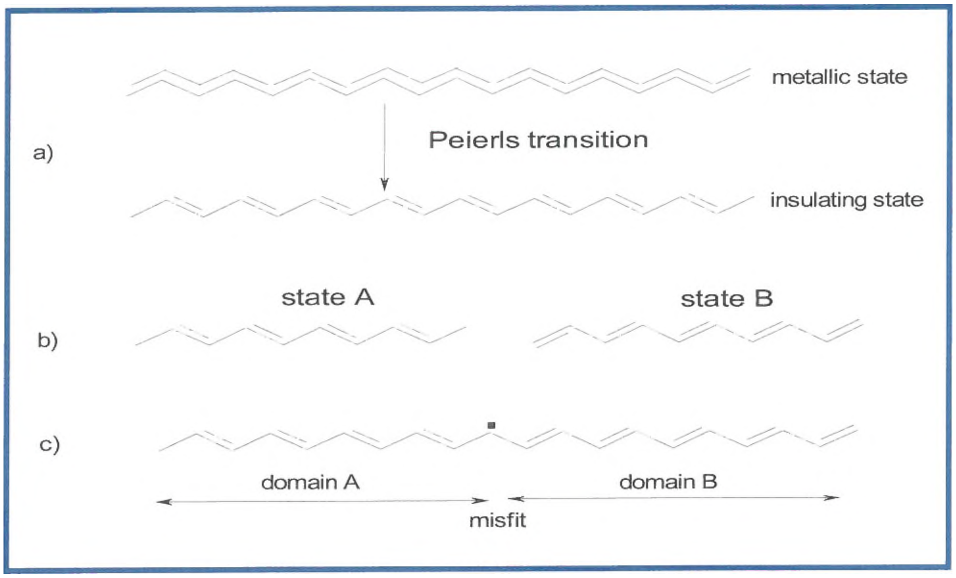

Fig 3 **a) Peierls transition of trans-polyacetylene from a conducting delocalized state to the energetically lower state with alternaa ting double bonds ; b) Two degenerate ground states of trans-polyacetylene ; c) When two different domains form on a polymer chain, a structural defect occurs at the border in the form of an unpaired electron.**

structural defect is called a soliton since it can move along the one-dimensional chain. The term soliton is not quite correct since these solitons do not pass through each other without interaction, but is generally used in the literature because they do not disperse while moving along the polymer chain. The existence of solitons can be experimentally verified by electron spin resonance since the dangling bond is a single electron with an unpaired spin.

The structure of polyacetylene depicted in Figure 3(c) is a simplification. Stafström and Chao have performed quantum mechanical calculations for a polyacetylene with 61 carbon atoms with a structural defect (soliton). The result of this calculation indicates that the soliton extends over about 20 lattice sites [15]. There is also a structural defect called an antisoliton, which is very similar to the soliton. However, if solitons are dangling bonds on odd numbered carbon atoms, antisolitons will be dangling bonds on even numbered sites. When a soliton and an antisoliton meet they will annihilate each other while generating energy. This is also why these solitons can be viewed as quasi particles. Conversely, excitation can lead to the formation of a soliton-antisoliton pair. Here, one of the double bonds will be broken because of the excitation, leaving dangling bonds on an odd- and an even-numbered carbon atom. Once the soliton and the antisoliton are formed, they can move apart before closing the double bond again. So far, only simple electrically neutral solitons have been considered. However, these unpaired electrons can participate in redox reactions (e.g. with impurities) that can lead to an addition or a removal of an electron. As a result, positively and negatively charged solitons are created, which however still separate two different domains. The electronic structure and chemical notation of these solitons are shown in Figure 4.

Pure conjugated polymers have a low concentration of solitons resulting in a low conductivity. After synthesis, polyacetylene has a concentration of about 400 radicals per 10^6 carbon atoms. However, it is possible to increase the number of solitons by various means, i.e. photogeneration, doping, and charge injection. If the polymer is subjected to light of appropriate wavelength, an electron can be excited to the π^* band from the π band which creates an electron-hole pair. If the lattice relaxes around this site, two solitons (e.g. positive and negative) are formed, which can move apart under the influence of an external field.

Alternatively, the two solitons can annihilate again radiatively giving rise to light emission. A different way of creating solitons is chemical doping. It was discovered in the late 1970s that the conductivity of doped polyacetylene increases significantly [16]. This behaviour was meanwhile confirmed for a number of other conjugated systems. If these polymers are doped with an appropriate dopant, a redox reaction takes place. One of the double bonds is broken and one electron is transferred to the dopant. This creates a neutral and a positive soliton in the polymer chain. By choosing an appropriate dopant, p- or n-type doping can be realized. As opposed to classical semiconductors, every dimer is a possible doping site and much higher doping concentrations are achievable. In polymers with a nondegenerate ground state, such as PPV, the two alternative sense of bond alternation do not have equivalent energies (Figure 5(a)). The soliton is not a stable excitation in these materials, since the high energy form can only exist over a finite length of the polymer chain. The charged excitations of a nondegenerate ground state

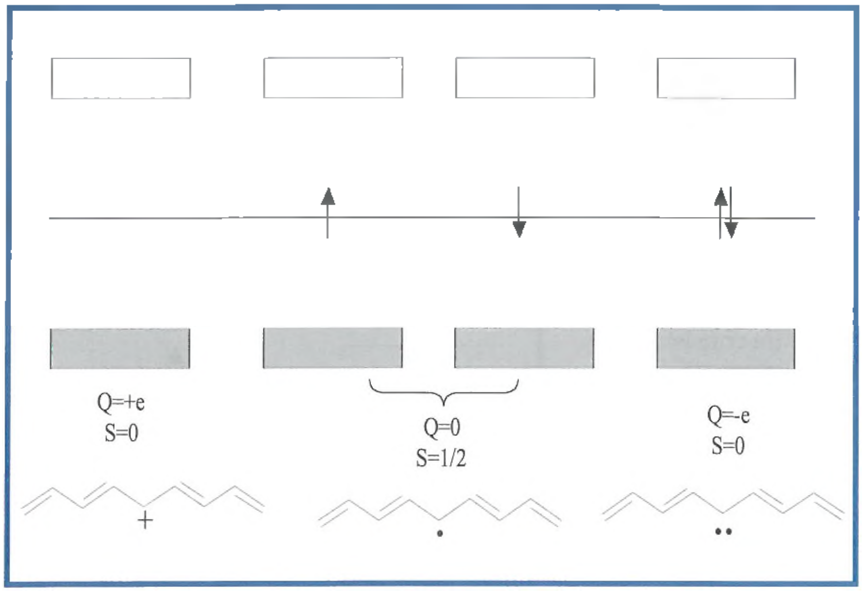

Fig 4 **Illustration for positive, neutral, and negative solitons**

polymer are called polarons or bipolarons and represent localized charges on the polymer chain with an accompanying local arrangement of bond alternation as shown in Figure 5 (b). A schematic representation of an intrachain exciton with relaxed chain geometry is shown in Figure 5(c).

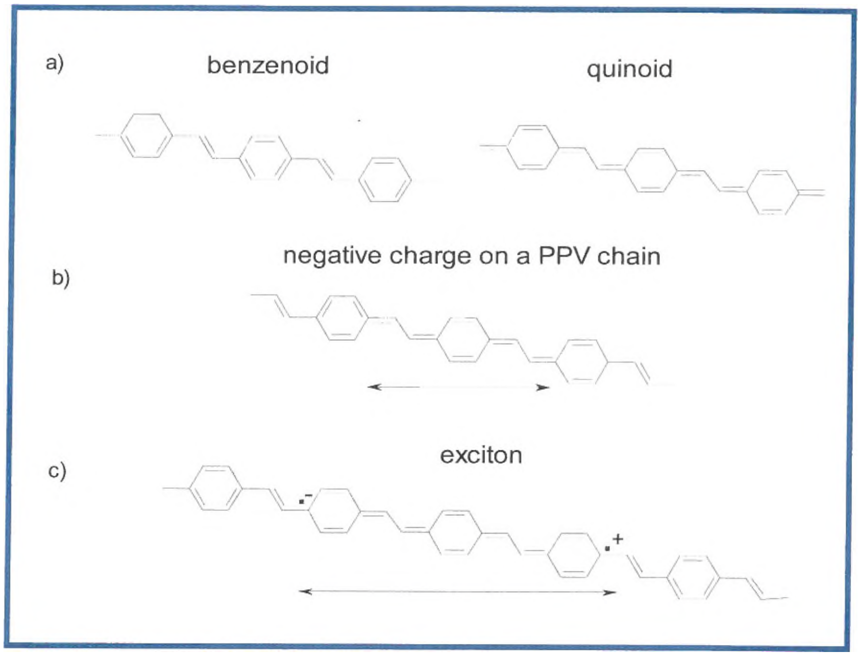

Fig 5 **a) Two possible forms of bond alteration in PPV: benzenoid and quinoid ; b) Negative charge on a PPV chain in a form of a quinoid ; c) A schematic representation of an intrachain exciton with relaxed chain geometry.**

These charged states could be considered as being equivalent to a confined soliton pair. The two nonbonding mid-gap soliton states form bonding and antibonding combination, thus producing two gap states symmetrically displaced about mid-gap (±ω) as shown in Figure 6. Depending on the occupancy of these states, positive bipolaron (bp^{2+}), positive polaron (p^{+}), polaron exciton, negative polaron (p^{-}) or negative bipolaron (bp^{2-}) can be generated [17]. Solitons, polarons, and bipolarons are essential models for understanding electronic conduction processes in polymers.

The organic polarons are somewhat similar to the inorganic polarons in that they are an electrically charged "particle" that causes the lattice to rearrange around it. The conjugated polymer however is a lattice in only one dimension. In addition, the motion of a polaron along the polymer involves the breaking and rearranging of chemical bonds that is a stronger interaction than the one for inorganic polarons. A typical soliton in polyacetylene extends over about 20 lattice sites and has an effective mass about 6 times that of a free electron [18]. When the conductivity of a polymer is investigated, it has to be kept in mind that the polaron mobility along the chain is just one of many contributing processes. A typical conducting polymer structure consists of many spaghetti-like-fibres, which are composed of many (100 to 1000) polymer chains. The explanation of the electrical conduction has to include all the intra-chain, interchain, and interfibre charge transport.

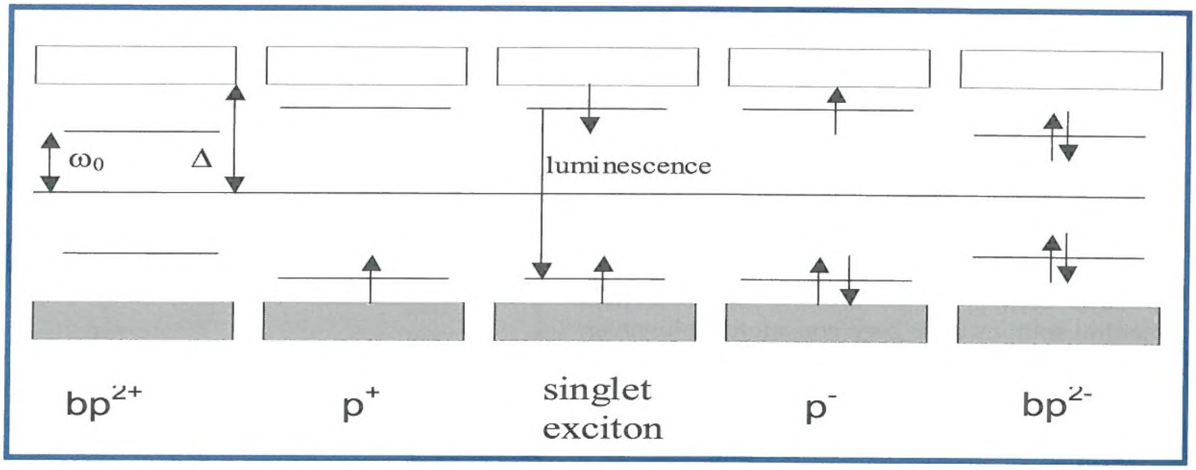

Fig 6 **Illustration of a polaron, bipolaron and singlet exciton energy levels in a nondegenerate ground state polymer (from [17]).**

Charge Injection and Transport in PLED

The generation of solitons and polarons can be realized by photo excitation, but more importantly, it can also be achieved through charge injection. For electric excitation, the polymer layer is sandwiched between metal electrodes with appropriate work functions such that one metal can efficiently inject electrons into the conduction band and the other can inject holes into the valence band (Figure 1). The lattice then relaxes around the carriers and solitons or polarons are formed. As depicted in Figure 1, the offset between the work function of cathode metal and the π*-band produces an energy barrier (ΔE_e) for electron injection, and that between the work function of anode and the π-band forms an energy barrier (ΔE_h) for hole injection. Under positive bias, charge carriers overcome (thermionic emission) or tunnel through the potential barrier via a combination of thermionic emission and Fowler-Nordheim tunnelling. Since there are several excellent articles describing and modeling these processes [17, 19-21], it is of use to emphasize, without getting into the theoretical details of these processes, that of prime importance is the control of the polymer-electrode interface in order to optimize the PLED performance. The nature of metal-organic interfaces has been studied both experimentally and theoretically [22-24]. The understanding of the metal/polymer or metal/organic interfaces is complicated by chemical reaction between the polymer and the metal layers during the metal deposition, and by metal and impurity diffusion at the interface region; these processes can cause metal Fermi level pinning, and impurity doping. Most experimental work still indicate that, in spite of these complications, the energy barriers at the electrode/polymer interfaces scale with the work functions of the electrode materials. The energy level offset at the interface is still a very useful parameter to estimate the charge injection efficiency.

Since conjugated polymers have very low charge mobility, the current in a specific type of device can be either injection limited or transport limited (space charge limited), depending on the magnitude of the potential barrier. In the injection-limited case, the contact barrier is the bottleneck in the charge transport process. This is usually true for devices with high contact barriers, in that it injects much fewer charge carriers than the polymer layer can transport. One of characteristics of injection-limited transport is that its J-E (current density-electric field) curve is not dependent on sample thickness, as found in the Fowler-Nordheim model for tunnelling injection and the Richardson-Schottky model of thermionic emission.

In the case of transport-limited case, one of the contacts needs to be either Ohmic or with sufficiently small energy barrier (<0.2 eV) that the contact is able to supply more charge carriers per unit time than the polymer can transport. The space charge limited current (SCLC) is the maximum current a polymer layer can conduct at a given electric field for a given type of charge carriers. Assuming an exponential distribution of traps, the general expression for the space charge limited current takes the form $J(SCLC) \alpha E^{n+1}/L^{n}$, where E is the electric field, L is the sample thickness, and n is a trap distribution related parameter. In the presence of charge trapping, n>1, a typical value is n=5. While in a trap-free case, n=1, the J-E curve is given by (Child's law):

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{E^2}{L}$$

where $\varepsilon_0 \varepsilon_r$ is the permittivity of the polymer material, μ the carrier mobility and L is the thickness of the device. In contrast to the injection-limited case, the *J-E* curve is clearly dependent on the sample thickness. This can be used as a very good criterion to identify whether the charge transport in a PLED is injection-limited or space charge limited. In practice, many devices demonstrate injection-limited behaviour at low-bias level and space charge limited current at high injection levels, and the field- and temperature-dependent charge mobility further complicate the modeling. Furthermore, the presence of only one type of charge carriers was considered for simplicity in the above discussion. However, in a polymer light emitting diode, electrons and holes are injected simultaneously from the cathode and the anode into a conjugated polymer layer. The current caused by both electrons and holes should be considered when thinking about space charge effects. The electron-hole capture process removes mobile charge carriers from the polymer layer and can therefore have a significant effect on the *J-E* characteristics of a PLED. For detailed treatment of these cases, readers are referred to Ref. [17,20].

Exciton Recombination and Decay Process in PLEDs

During operation of a PLED, electrons are injected from the cathode into the π^* band by forming radical anions and holes are injected from the anode to the π band by forming radical cations. The resulting charged states migrate from polymer chain to polymer chain under the influence of the applied electric field. When a radical anion and a radical cation meet on a single conjugated segment (bimolecular charge recombination), they combine to form a neutral excited state - singlet (S=0) or triplet (S=1) exciton. Whereas quantum mechanical selection rules allow for light emission from electron-hole recombination on the singlet excited molecular state as in fluorescence, it does not allow for triplet exciton recombination [25]. As the electron-hole recombination with uncorrelated spins is three times as likely to yield spin symmetric (S=1) rather than spin asymmetric state (S=0), the maximum internal quantum efficiency of the PLED using fluorescence as emission mechanism is capped at 25% (photon/electron). Although the decay of a triplet state is "forbidden" by conservation of spin, efficient and rapid electrophosphorescence can be achieved in some organometallic compounds or polymers with heavy metal atoms in the centre favouring strong spin-orbit coupling [26] that mixes singlet and triplet states leading to the radiative recombination of the triplet state (S=1). The probability of intersystem crossing from singlet to triplet excited states is also increased. As a result, the lowest triplet state is efficiently populated, and produces efficient phosphorescence emission. A challenge in using phosphorescent materials is the diffusion lengths of the triplet excitons due to their long lifetime. The use of proper exciton blocking layers such as bathocuproine (2,9-dimethyl-4,7 diphenyl-1,10-phenanthroline) [27] is required to confine the excitons within the emissive layer. Lane *et al.* [28] obtained an external device efficiency of 3.5% in a poly(9,9-dioctylfluorene) PLED doped with 4% of PtOEP. These results demonstrate the potential of using phosphorescent dopants in organic and polymer light emitting devices, and the possibility of obtaining devices with close to 100% internal efficiency. In the above discussion, it was assumed that singlet and triplet intramolecular excitons are the only end products of charge recombination; this assumption is not valid for some PLED device structures or layer combinations where interchain exciplexes can be formed.

SOME PRACTICAL ISSUES WITH PLED DESIGN AND FABRICATION

Polymeric Light Emitting Device Structures

To achieve high luminescence efficiency, one obvious choice is to use polymers with high photoluminescence efficiency as emitters. A polymer light emitting device structure comes in two varieties: single-layer (Figure 1) and multi-layer. The internal quantum efficiency of a PLED is defined as the ratio of the number of photons generated within the device to the number of electrons flowing in the external circuit. An unbalanced charge injection will result in an excess of one type of charge carrier, i.e. a current that does not contribute to the light emission. As a result, the presence of a contact barrier that limits the injection of charge carriers or leads to

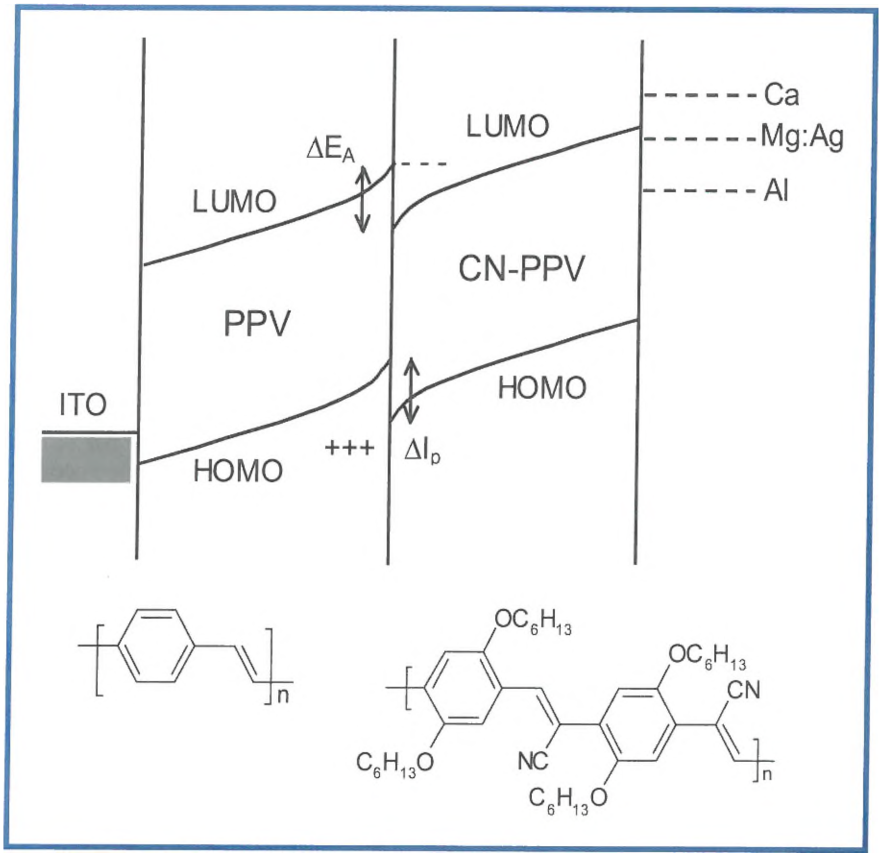

Fig 7 **A schematic energy level diagram fro a PPV/CN-PPV double-layer PLED under forward bias. The energy offsets between the HOMO and LUMO of PPV and CN/PPV confine the holes and electrons at the interface region (from [33]).**

unbalanced charge injection will result in low power efficiency and device quantum efficiency [17,29,30]; therefore it is necessary to reduce the injection barrier and achieve a good balance between electron and hole currents for efficient exciton formation in the emissive layer. However, it is difficult to balance the injection and transport of the two types of charge carriers in a single-layer device, over a reasonable voltage range. One approach to increase the quantum efficiency of single layer PLEDs is to dilute the charge transport materials to slow down carrier motion inside the PLED, enhancing the steady state charge density, and thus the efficiency of exciton formation [31,32].

To obtain higher device efficiency, at least two layers are necessary in the design of the light emitting device, separating the transport of electrons and holes and providing confinement for hole-electron recombination. Figure 7 shows a schematic energy level diagram for a double-layer PLED under forward bias [33]. In this device, PPV was used as hole-transport layer and CN-PPV was used as both electron-transport and emitting layer. At the interface between the two polymers, there are 0.9 eV (ΔE_A) and 0.6 eV (ΔI_p) offsets in LUMO and HOMO levels respectively. Under forward bias, holes injected from the ITO into the HOMO of the PPV layer move to the heterojunction where they are confined; electrons injected from the cathode also move to and are confined at the heterojunction. Tunneling across one or other barrier will form excitons. For this device configuration, the hole tunnels into the CN-PPV and electroluminescence originates from CN-PPV. External quantum efficiency as high as 2.5% was obtained for PPV/CN-PPV double-layer devices. As shown in Figure 7, a double layer structure is very similar to the p-n junction light emitting diode, although we are considering only an undoped intrinsic semiconductor system. However, the fabrication of double or multi-layer polymer structures is not a trivial task. In solution-based thin film fabrication processes (spin-coating, screen-printing, ink-jet printing), solvent compatibility of successive layers can lead to swelling or dissolution of the first layer. Since a multi-layered device structure is a critical step in fabricating highly efficient PLEDs, much research effort has been devoted to this area. Researchers have developed different strategies to fabricate multi-layered PLED structures using 1) polymer materials of very different solubility in multi-layered structure, 2) plastic lamination processes or cross-linkable polymer layers, as well as, 3) chemical vapor deposition to avoid the use of solvents. Bernius *et al.* [34] reported the use of fluorene copolymers with carboxylic acid substituents for the hole-transport layer, as these are soluble in polar solvents like DMF, but practically insoluble in aromatic hydrocarbons such as toluene and xylene. An electron-transport and emitting fluorine polymer layer was then spin-coated on top of this layer using a xylene solution. A double layer structure with sharp polymer-polymer interface was successfully produced using this method. Hay *et al.* have developed a new series of arylamine-based hole-transport polymer [35,36] that can only be dissolved in strong organic solvents such as chloroform, for use in double layer PLEDs fabrication. By using electron transport polymers that are soluble in toluene, double layered polymer blue light emitting devices have been successfully fabricated [37]. Yang and his co-workers [38] recently reported a low temperature lamination method using a 'template activated surface process' to fabricate high performance double layer blue and red-emitting PLEDs at a temperature much lower than the Tg of the polymers used in their devices. The invention of cross-linkable oligo- and poly(dialkylfluorene)s series [39-41] certainly enabled the multi-layer PLED fabrication using solution processable and thermally cross-linkable polymeric or oligomeric materials. As an alternative approach for making multi-layered polymer devices, Murata [42] recently reported a two-layered polymer light emitting device prepared by a vapor deposition polymerization process, which has the advantage of solvent-free fabrication environment, good thin film uniformity, and minimum contamination. The fabrication cost could still be problematic, and the vapor phase polycondensation reaction used in his experiment could be difficult to apply to other polymer systems.

In addition to better exciton confinement and dedicated charge-transport layers, a multi-layer fabrication process is also needed for the passivation of ITO substrates to block elemental diffusion from the ITO layer to the electroluminescent material (ELM). It has been found that during PLED operation, oxygen and metallic ions are released from the ITO matrix into the electroluminescent layer under long-term action of the applied electric field, which typically can reach 10^6-10^7 V/cm. This leads to oxygen poisoning of the polymer layer [43] and produces metallic quenching sites within the ELM. Bernius *et al.* [44] have experimentally demonstrated mass loss from the ITO layer into the active pixel area due to the elemental depletion of indium in the remaining ITO. Therefore it is necessary to buffer the active EL layer from the metallic ion and oxygen contamination originating in the ITO substrate. Conducting polymers such as polyaniline (PANI) [45,46] and poly-(3,4-ethylene dioxythiophene) (PEDOT) have been successfully used for this purpose.

Another important factor to be considered for increasing the device quantum efficiency and stability is the surface treatment and interface engineering at the anode/polymer and cathode/polymer interfaces. Although reducing the charge injection barriers is an important issue in OLED or PLED fabrication, a unilateral lowering of the injection barrier for either holes or electrons will not necessarily increase the device quantum efficiency as this tends to further unbalance the electron and hole currents in some cases. Therefore, we should first consider reducing the height of the higher charge injection barrier reaching balanced charge injection with a concomitant reduction in barrier heights. Researchers have used low work function metals (Ca, Ba, Sr, Mg, Al) or metal alloys (Mg: Ag, Al:Li) as cathode materials to reduce the electron injection barrier. On the anode side, the choice is rather limited, although transparent conducting oxides, other than ITO have been used, e.g. GaInO, and ZnInO. However, ITO remains a prime material of choice for use as anode material for OLEDs and PLEDs, due to its good conductivity and transparency. UV ozone treatment or oxygen plasma treatment have been found effective in increasing the work function of the ITO surface due to the removal of adsorbed hydrocarbons on the ITO surface; in addition, the oxygen enrichment of the ITO surface can modify the surface conductivity and increase the work function [47]. Zuppiroli *et al.* [48,49] demonstrated that, by chemically attaching the electroactive polymer to the ITO electrode to form an ordered monolayer, the electric field produced by the assembled monolayer will effectively increase the surface work function "seen" by holes, so that hole injection is enhanced. The importance of balanced charge injection to the device efficiency is clearly demonstrated in a recent publication of Campbell *et al.* [50].

Polymers Used For Electroluminescent Devices

The electroluminescent polymer used in PLEDs is critical to the device performance. Processability, material purity, thermal and oxidative stability, emission colour, charge carrier mobility, and luminescence efficiency are the main concerns when designing or choosing an electroluminescent polymer. Our intention here is to briefly introduce several kinds of frequently used electroluminescent polymers, their advantages and disadvantages. For details about these materials and syntheses, readers are referred to several excellent review articles on these materials [34,44,51,52]. PPV, first synthesized by Wessling at Dow Chemical in 1968, has a π-π^* energy gap of 2.5 eV, and is not soluble in common solvents. It was the first conjugated polymer used for polymer light emitting devices [12]. Special processing steps are needed in order to make polymer thin films suitable for EL applications. The incorporation of PPV into a PLED is typically performed via a soluble precursor polymer that is spin-coated into thin films and thermally converted to PPV. The quality of these PPV films strongly depends on the individual processing steps of the precursor. The need to convert precursor films to PPVs presents additional complexity in the processing of PLED devices and offers a variable that can significantly affect the overall device performance. PPV films have also been prepared using a self-assembly, layer-by-layer process [53-55] or a Langmuir-Blodgett technique [56,57]. By introducing side-chains into the PPV skeleton, one can modify not only the electronic properties of PPV (such as the energy band gap, HOMO, and LUMO levels), but also increase its solubility in common solvents. In 1991, Heeger and Braun [58] at the University of California at Santa Barbara announced the EL application of a soluble derivative of PPV, poly[2-methoxy-5-(2'-ethythexyloxy)-1,4-phenylenevinylene] or MEH-PPV (Figure 8). MEH-PPV has a π-π^* electronic energy gap of 2.2 eV, red-shifted from that of PPV. An external efficiency of 1% was obtained in a single-layer device configuration (ITO/MEH-PPV)/Ca. Due to the dialkoxy side chain, MEH-PPV offered the advantage of being soluble in conjugated form in organic solvents, thus providing much better processability as compared with PPV. However, because of its susceptibility to photo-oxidation, MEH-PPV's commercial application remains questionable. A variety of PPV derivatives containing long alkyl and alkoxy chains, cholestanyloxy and oligoethenyloxy substituents by polycondensation, have been synthesized by Wittig-, or Heck-type reactions (Figure 8). PPV derivatives with at least one long solubilizing alkoxy side chain are soluble in organic solvents such as chloroform or THF. As compared to PPV, their emission peak is usually red-shifted. The long side chains in these derivatives quite often appear to suppress the formation of non-emissive relaxation sites, a distinctive advantage with regard to the fluorescence and electroluminescence efficiencies of these polymers. However, the introduction of silyl substituents not only increased the solubility, but also produced a wider band-gap for green light emission [59,60].

Efficient polymer emitters of three basic colours, i.e., red, green and blue are essential for the realization of full-colour displays. Blue emission requires a HOMO-LUMO energy gap of about 2.7 to 3.0 eV. In 1992, Leising and his co-workers [61] reported for the first time on blue electroluminescence from PLEDs containing poly (p-phenylene) (PPP) (Figure 8). The external efficiency obtained for that ITO/PPP/Al device was ~0.05%. Due to the lack of vinylene linkage between the phenyl rings, the overlap of the π-electron wave functions is weaker in PPP systems. Therefore, paraphenylene polymers show a higher LUMO-HOMO energy difference of about 3.0 eV, and represent a class of conjugated polymers with potential applications in blue EL devices. PPP and its derivatives also have extraordinarily high thermal and oxidative stabilities. However, similar to the situation with PPVs, most PPP polymers are insoluble and intractable. The research activities in the PPP field have concentrated on developing PPP films using soluble and thermally convertible precursor polymers, as well as synthesizing soluble PPPs. In an effort to improve processability, PPP derivatives bearing solubility-enhancing groups like alkyl, alkoxy, aryl or perfluoralkyl side chains have been synthesized and used as active materials in PLEDs.

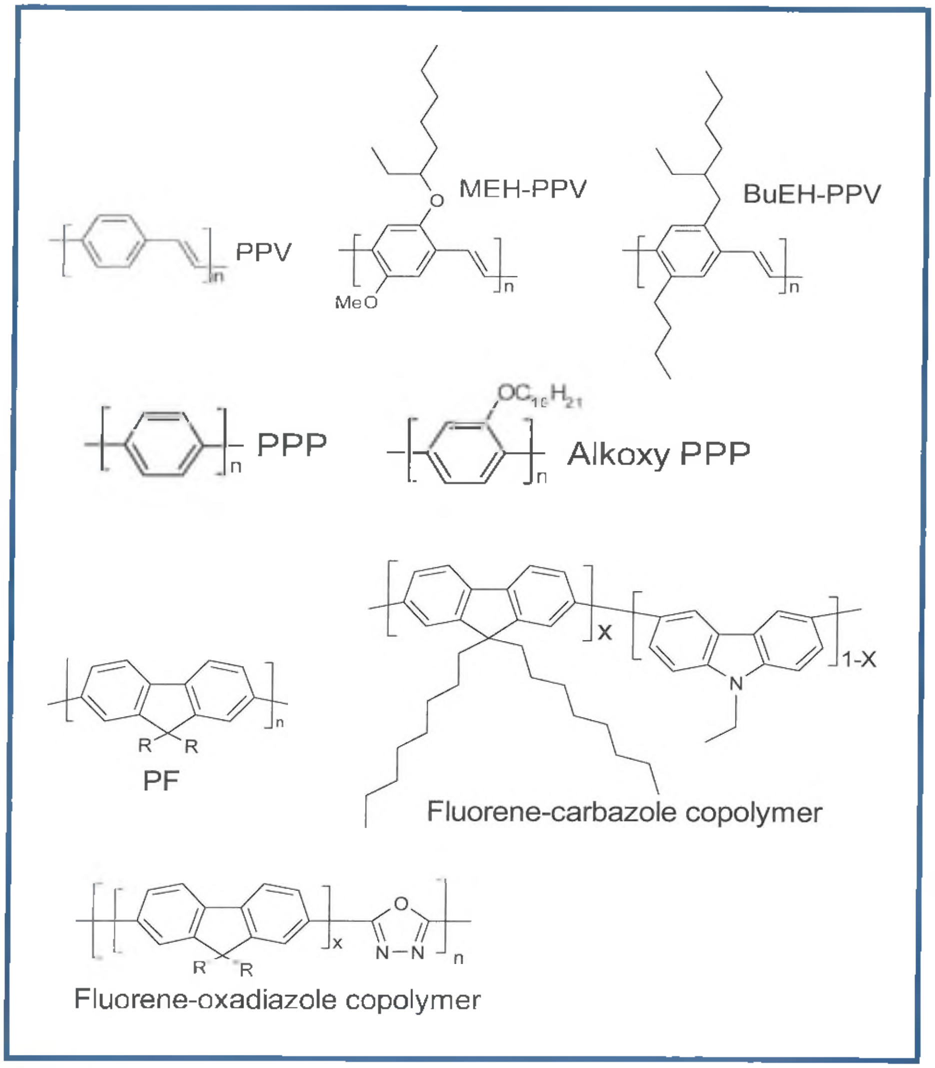

Fig 8 Molecular structures of PPV, PPP, PF and some of their derivatives.

Wide band gap polyfluorenes (PF) (Figure 8) were first synthesized by Fukuda and co-workers using the ferric chloride oxidative routine about a decade ago [62,63], and were introduced as a potential blue emitting layer for polymer light emitting devices [64-66]. These materials demonstrate extremely high photoluminescence efficiencies both in solution and in solid state films [67,68], with emission spectra primarily in the blue region. They also demonstrate better photostability, resistance to photo-oxidation and thermal stability as compared to PPVs [67,69,70]. Polyfluorene and its derivatives are now attracting considerable interest as emitting materials for PLEDs [34,44,71], since they are the only family of conjugated polymers that can emit colours covering the entire visible spectral range with high efficiency and low voltage [72-74]. However, chain aggregation in the solid film tends to degrade the device performance [39,70,75], leading to a red-shifted fluorescence or electroluminescence, and reduced intensity by exciton migration and relaxation through lower energy excimer traps [70,75]. This is probably due to its rigid-rod structure, which tends to form a nematic type of packing in the bulk making it prone to chain aggregation. To depress chain aggregation, enhance fluorescence efficiency, and increase the hole-transport abilities, Xia *et al.* [76] introduced carbazole units into the polyfluorene chain by forming 9:1 and 7:3 copolymers with the carbazole group at the 3,6 positions, thus introducing disorder in the polymer backbone. The resulting copolymers demonstrated better spectral properties both in solution and in thin film, and improved thermal and UV stability as compared to homopolymers. Polymerizing fluorene monomers with various comonomers have yielded a wide range of copolymers [34,73,77-79]. Red, green and blue polymer light emitting diodes have been realized by using fluorene-based copolymers [80]. Many of fluorene copolymers demonstrated improved photoluminescence efficiency, charge transport properties and higher thermal and oxidative stability [81]. Contrary to PPV and related materials, polyfluorene has poor hole-transport abilities. In conventional PLED devices using fluorene polymers as emitters, electrons appear to be the majority charge carrier in the devices. The device performance can be significantly improved if an appropriate hole-transporting layer is incorporated into the device structure.

PERSPECTIVE IN POLYMER BASED LASER STRUCTURES

Laser devices can be found in almost every corner of our daily life: at our homes, in telecommunication, medicine, entertainment, as well as in science and technology. A variety of laser sources are available, e.g. gas lasers, dye lasers, and semiconductor lasers. Many conjugated organic molecules are highly luminescent in solution, and have large Stokes shifts between the absorption and fluorescence shifting the emission away from the absorption edge, making the self-absorption minimal and facilitating population inversion. Conjugated organic molecules have been used in dye lasers as active media to produce tuneable laser emission over a wide spectral range for more than 30 years [82]. In 1961 (one year after the first laser was invented), Brock *et al.* [83] suggested that conjugated organic molecules doped in a host crystal (matrix) might be interesting for solid-state laser applications. The use of a host crystal was to dilute the molecules to avoid the common issue of concentration quenching in dye-lasers. Lasers based on organic dye molecules doped into passive solid-state matrices were demonstrated nearly 10 years later [84-86]. Due to the rapid material degradation caused by poor photochemical stability of the dye molecules, the application of these solid-state dye lasers was very limited. In today's information technology sector, the solid-state semiconductor lasers are predominant laser sources. Although significant progress has been made in inorganic compound semiconductor diode lasers, a significant part of the visible spectral range is not readily accessible by the most commonly used III-V semiconductor lasers. The high quantum efficiency and the easily tunable emission colours demonstrated in the recent organic and polymeric electroluminescent devices have stirred up research interest in electrically pumped solid-state organic or polymeric lasers.

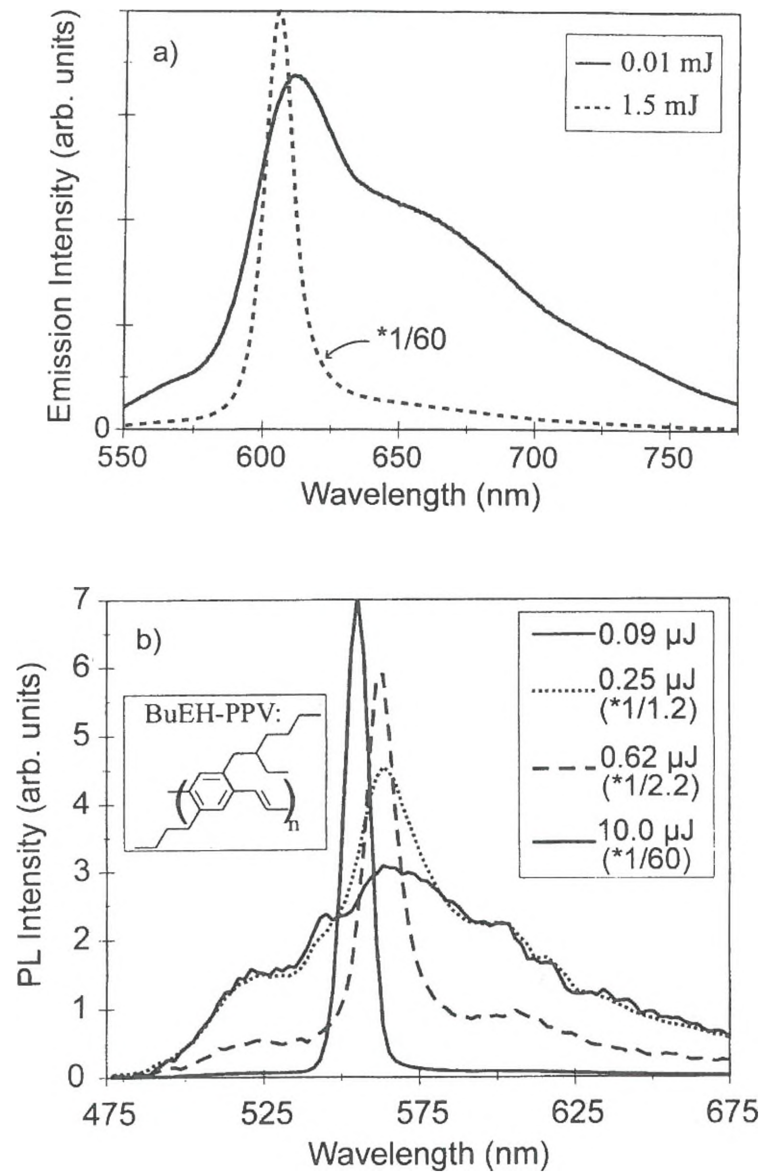

Fig 9 a) The emission spectra of a freestanding film of a blend system of 0.9% MEH-PPV in polystyrene with $\sim 10^{11}$cm^{-3} TiO_2 nanoparticles at two different excitation intensities. The broad emission spectrum of MEH-PPV collapsed into a narrow emission line above a certain threshold (from ref. [92]). Laser pulses of 20 ns duration at 532 nm was used as optical excitation ; b) The gain narrowing observed for a 210 nm thick film of BuEH-PPV spin-coated on a glass substrate at different excitation energies. Laser pulses of 10 ns duration at 435 nm was used as optical excitation. (from ref. [90]).

In the field of conjugated molecular materials, the work has been concentrated on laser dye-doped molecular electroluminescent material systems. In 1997, Kozlov *et al.* [87] demonstrated laser action in an optically pumped molecular semiconductor system, tris-(8-hydroxyquinoline) aluminium (Alq_3) doped with 2.5% DCM dye. In their experiment, an emission output threshold as a function of pumping power, gain narrowing, strong polarization in emission, spatial coherence, and the laser cavity resonance were clearly demonstrated. Laser action was also reported in 2-napthyl-4,5-bis(4-methoxyphenyl)-1,3-oxazole (NAPOXA) doped with DCM II [88,89]. Since then optically pumped solid-state organic lasers have been investigated by many research groups, aiming at electrically pumped organic semiconductor lasers. Various types of laser structures suitable for organic lasers like microdisks and spheres, vertical cavity surface-emitting lasers, distributed Bragg reflectors (DBRs), and distributed feedback (DFB) structures have been applied to optically pumped organic lasers. However, laser action in many dye-doped organic systems can be characterized by low lasing threshold ($\sim 1\ \mu J/cm^2$), which corresponds to a carrier density of $1.5 \times 10^{12}\ cm^{-2}$. Assuming an internal device efficiency of 5-10% for electroluminescence, the transient current densities necessary to reach the threshold for lasing are estimated to be around a thousand amperes per square centimetres [87,90]. The transient current density of this order of magnitude poses a significant challenge to the realization of electrically pumped diode lasers based on organic semiconductors characterized by low charge carrier mobility. This difficulty might be overcome by developing more efficient electroluminescent organic semiconductors with high charge mobility, or by using innovative device structures. The dilemma between the required current density and the inability of organic or polymeric materials to carry high-density electric current is a major obstacle for realizing diode lasers. In that sense, hybrid inorganic-organic diode laser structures may find their use in this field.

Unlike small conjugated organic molecules, which have been used as chromophores in dye lasers for decades, laser action from conjugated polymers was first reported in 1992 by Moses [91] in a liquid-dye laser configuration, using MEH-PPV (poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) in xylene or chloroform (replaced commonly used dyes). The first report on gain narrowing in a solid conjugated polymer was made by Hide and co-work-

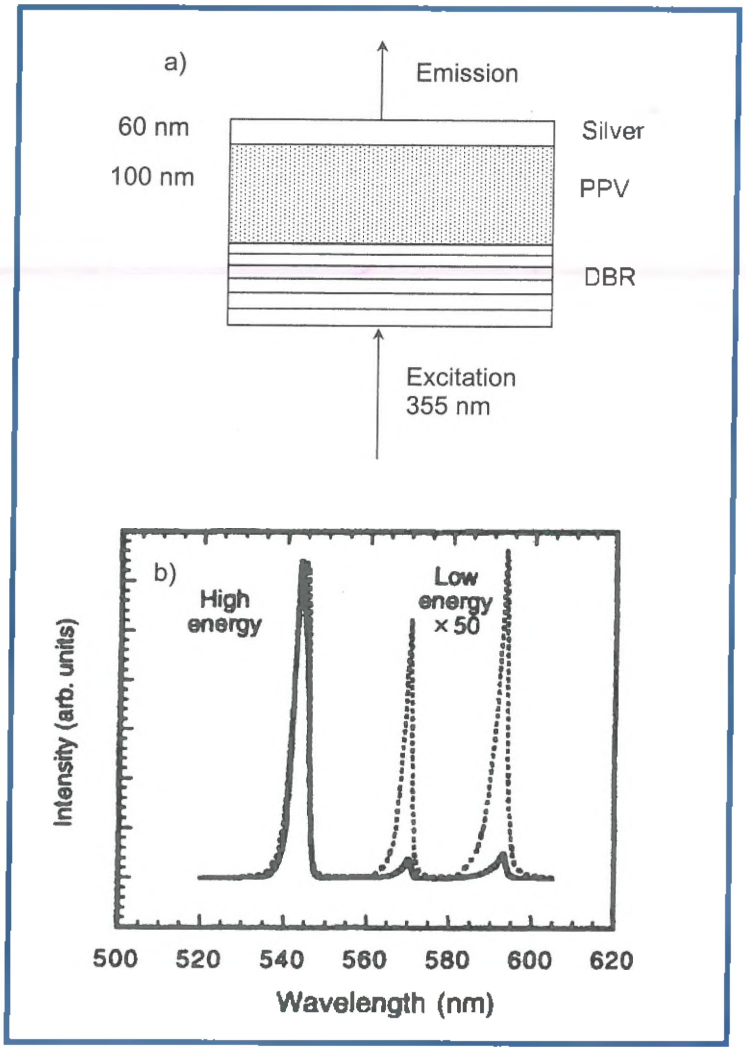

Fig 10 a) A microcavity laser structure is formed by inserting a PPV film between a highly reflective distributed Bragg reflector and a thermally evaporated silver mirror ;
b) Emission spectra of the microcavity at excitation energies of 0.05 μJ (dashed line) and 1.1 μJ (solid line), respectively. The lasing action was demonstrated by the non-linear behaviour of different modes. The device was pumped at 355 nm with pulse duration between 200-300 ps. (From ref. [103]).

ers [92] in 1996 when they blended titanium oxide nano-particles into a MEH-PPV/polystyrene film; the randomly distributed titanium oxide nano-particles scattered the light emitted by the MEH-PPV in such a way that the feed back loop needed for lasing was provided. Figure 9 shows the measured emission spectra for two different excitation intensities. As shown in this figure, the broad emission spectrum of MEH-PPV collapsed into a narrow emission line when the pump intensity is increased above a certain threshold, indicating a gain narrowing due to stimulated emission.

Although the titanium nano-particles effectively increased the length that spontaneously emitted photons propagate inside the gain media so that the gain narrowing can be achieved at lower excitation power, this approach has some disadvantages for device applications, e.g. charge transport is hampered by the dielectric nano-particles, and the emission does not show any directionality due to the multiple scattering. Later that year, Hide *et al.* [90] and Frolov *et al.* [93,94] reported line narrowing from films of a variety of PPV derivatives suggesting possible lasing without a resonant structure. Upon increasing the pump energy above threshold, the broad emission spectrum collapsed into a narrow emission line. Strictly speaking, the mechanism behind this type of spectral narrowing is different from lasing. Most researchers now agree that the spectral narrowing of the emission in conjugated polymer films at high excitation is a general phenomenon, and is caused by amplified spontaneous emission (ASE). The ASE occurs even when the gain coefficient is small since the spontaneously emitted photons are wave-guided in the films and thus travel a long distance through the gain medium, where they are amplified by stimulated emission. In the same year, Tessler *et al.* [95] made a first attempt to combine gain narrowing upon high excitation with a resonator structure that provides positive feedback in order to achieve true lasing action in conjugated polymer films (Figure 10 (a)). A microcavity laser structure was formed by inserting a spin-coated PPV (poly(p-phenylenevinylene)) film (non-blended, neat film) between a highly reflective distributed Bragg reflector (DBR) and a thermally evaporated silver mirror. The two mirrors confine the light wave and lead to discrete optical modes inside the cavity. The lasing action was demonstrated by the non-linear behaviour of different modes (Figure 10(b)); at higher excitation, the spectrum fully collapsed into the mode with the highest gain. This non-linear effect was also accompanied by an enhanced directionality in the emission. This was the first time that a polymer laser was based on a material that could support current densities up to a thousand amperes per square centimetre [96,97]. The disadvantage of this microcavity design is that the small gain length per reflection between the two mirrors leads to higher threshold values. Metal mirrors are usually very lossy and the use of highly reflective dielectric mirrors on both sides of the cavity can effectively reduce the threshold [98,99]. An effective way to increase the gain length in a device is to use a geometry with the lasing process occurring in the lateral direction, but that also eliminates a major advantage for using polymers devices, i.e. low-cost, large emission area. The distributed feedback (DFB) laser structures have this kind of feature. A DFB structure achieves optical feedback in the lateral direction by the use of a periodic modulation of the refractive index. They were first developed for films containing organic dyes [85] and have since been used extensively in traditional semiconductor lasers and small molecule organic laser structures [88,100]. The effect of the DFB structure in reducing the threshold for optically pumped organic or polymer lasers has been clearly demonstrated [101,102].

Although optically pumped molecular and polymer lasers have become a reality, whether the advance in optically pumped lasers will result in stable electrically pumped diode laser remains a question. It is very possible that the first generation of organic or polymer diode lasers will be a hybrid type, which uses the easily tunable emission property of conjugated organic molecules or polymers and the excellent charge transport and thermal stability of inorganic semiconductors such as GaN, InGaN, etc.

SUMMARY

This brief review of the development of polymer light emitting materials and devices could not do justice to the tremendous body of work which has been done during the last fifteen years. Thanks to the concerted efforts of teams of chemists, physicists and engineers, the field has progressed from a tantalizing laboratory result to bright displays in cellular phones and audio equipment. The stability and reliability issues which dominated the early discussions of market penetration, have been addressed as stable materials have been synthesized and purified, fabrication processes and multiple layer device structures have been devised to avoid known degradation mechanisms. The road to developing high performance electroluminescent materials has taken us back to the elucidation of carrier transport in organic and polymeric materials as this may provide the key to designing processable polymeric semiconductors with high luminescent efficiency and high charge carrier mobility for light emitting and laser applications.

REFERENCES

1. G. Destriau, *J. Chem. Phys* **33,** 587 (1936).
2. M. Pope, H.P. Kallman, and P. Magnate, *J. Chem. Phys.* **38,** 2042 (1963).
3. W. Helfrich and W.G. Schneider, *Phys. Rev. Lett.* **14,** 229 (1965).
4. W. Helfrich and W.G. Schneider, *J. Chem. Phys.* **44,** 2902 (1966).
5. G.G. Roberts, M. McGinnity, W.A. Barlow, and P.S. Vincett, *Solid State Commun.* **32,** 683 (1979).
6. P. S. Vincett, W. A. Barlow, R. A. Hann, and G. G. Roberts, *Thin Solid Films* **94,** 171 (1982).
7. C.W. Tang and S.A. Van Slyke, *Appl. Phys. Lett.* **51,** 913-915 (1987).
8. G. Horowitz, D. Fichou, X. Peng, Z. Xu, and F. Garnier, *Solid State Commun.* **72,** 381 (1989).
9. D. Fichou, G. Horowitz, Y. Nishikitani, and F. Garnier, *Synth. Met.* **28,** C723 (1989).
10. D. Fichou, G. Horowitz, Y. Nishikitani, and F. Garnier, *Chemtronics,* **3,** 176 (1988).
11. G. Horowitz, D. Fichou, and F. Garnier, *Solid State Commun.,* **70,** 385 (1989).
12. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, and A.B. Holmes, *Nature,* **347,** 539-41 (1990).
13. Peierls, (Clarendon Press, Oxford, 1955).
14. C.R. Fincher, C.-E. Chen, A.J. Heeger, and A.G. MacDiarmid, *Phys. Rev. Lett.,* **48,** 100-104 (1982).
15. S. Stafström and K.A. Chao, *Phys. Rev.,* **B29,** 2255–2266 (1984).
16. C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, *Phys. Rev. Lett.,* **39,** 1098-1011 (1977).
17. C. Greenham and R.H. Friend, *Solid State Physics,* **49,** 1-149 (1995).
18. W.P. Su, J.R. Schrieffer, and A.J. Heeger, *Phys. Rev. Lett.,* **42,** 1698-1701 (1979).
19 I.D. Parker, *Proceedings of the SPIE The International Society for Optical Engineering,* **2144,** 51-64 (1994).
20. P.W.M. Blom and M. Vissenberg, *Materials Science & Engineering R: Reports,* **R27,** 53-94 (2000).
21. H. Bassler, *Polymers For Advanced Technologies,* **9,** 402-418 (1998).
22. W.R. Salaneck and J.L. Bredas, *Adv. Mater.,* **8,** 48 (1996).
23. H. Ishii, K. Sugiyama, D. Yoshimura, E. Ito, Y. Ouchi, and K. Seki, *IEEE Journal of Selected Topics in Quantum Electronics,* **4,** 24-33 (1998).
24. K. Seki, E. Ito, H. Oji, D. Yoshimura, N. Hayashi, Y. Sakurai, Y. Hosoi, T. Yokoyama, T. Imai, Y. Ouchi, and H. Ishii, (2001).
25. M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, New York, 1999).
26. M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, and S.R. Forrest, *Nature,* **395,** 151-4 (1998).
27. Y. Kijima, N. Asai, and S. Tamura, *Japanese Journal of Applied Physics Part 1 Regular Papers Short Notes and Review Papers,* **38,** 5274-5277 (1999).
28. P.A. Lane, L.C. Palilis, B.-D.F. O, C. Giebeler, A.J. Cadby, D. G. Lidzey, A.J. Campbell, W. Blau, and D.D.C. Bradley, *Physical Review B,* **63,** 235206 (2001).
29. R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R N. Marks, C. Taliani, D.D.C. Bradley, S.-D.A. Dos, J.L. Bredas, M. Logdlund, and W.R. Salaneck, *Nature,* **397,** 121-128 (1999).
30. J.R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, and A. Stocking, *Science,* **273,** 884-8 (1996).
31. H. Kurczewska and H. Bassler, *Journal of Luminescence,* **15,** 261-266 (1977).
32. U. Albrecht and H. Bassler, *Chemical Physics,* **199,** 207-14 (1995).
33. D.R. Baigent, N.C. Greenham, J. Gruner, R.N. Marks, R.H. Friend, S.C. Moratti, and A.B. Holmes, *Synth. Met.,* **67,** 3-10 (1994).
34. M. Bernius, M. Inbasekaran, E. Woo, W.S. Wu, and L. Wujkowski, *Journal of Materials Science Materials in Electronics,* **11,** 111-116 (2000).
35. F. Santerre, I. Bedja, J.P. Dodelet, Y. Sun, J. Lu, A.S. Hay, and M. D'Iorio, *Chem, Mater.,* **13,** 1739-1745 (2001).
36. J.P. Lu, K. Miyatake, A.R. Hlil, and A.S. Hay, *Macromolecules,* **34,** 5860-5867 (2001).
37. V. Jousseaume, T. Maindron, Y. Wang, J.P. Dodelet, J. Lu, A.R. Hlil, A.S. Hay, and M. D'Iorio, *Thin Solid Films,* **416,** 201-207 (2002).
38. T.F. Guo, S. Pyo, S.C. Chang, and Y. Yang, *Adv. Funct. Mater.,* **11,** 339-343 (2001).
39. G. Klarner, J.I. Lee, V.Y. Lee, E. Chan, J.P. Chen, A. Nelson, D. Markiewicz, R. Siemens, J.C. Scott, and R.D. Miller, *Chem, Mater.,* **11,** 1800-1805 (1999).
40. J.P. Chen, G. Klaerner, J.I. Lee, D. Markiewicz, V.Y. Lee, R.D. Miller, and J.C. Scott, *Synth. Met.,* **107,** 129-135 (1999).
41. D. Marsitzky, J. Murray, J.C. Scott, and K. Carter, *Chem. Mater.,* **13,** 4285-4289 (2001).
42. H. Murata, *Synth. Met.,* **121,** 1679 (2001).
43. J.C. Scott, J.H. Kaufman, P.J. Brock, R. DiPietro, J. Salem, and J. A. Goitia, *J. Appl. Phys.,* **79,** 2745-51 (1996).
44. M.T. Bernius, M. Inbasekaran, B.-J.O, and W.S. Wu, *Adv. Mater.,* **12,** 1737-1750 (2000).
45. Y. Yang and A.J. Heeger, *Appl. Phys. Lett.,* **64,** 1245-7 (1994).
46. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. Reynolds, *Adv. Mater.,* **12,** 481 (2000).
47. D. Milliron, I. Hill, C. Shen, A. Kahn, and J. Schwartz, *J. Appl. Phys.,* **87,** 572 (2000).
48. F. Nuesch, L. SiAhmed, B. Francois, and L. Zuppiroli, *Adv. Mater.,* **9,** 222& (1997).
49. L. Zuppiroli, L. Si Ahmed, K. Kamaras, F. Nuesch, M.N. Bussac, D. Ades, A. Siove, E. Moons, and M. Gratzel, *European Physical Journal,* **B11,** 505-512 (1999).
50. A.J. Campbell, D.D.C. Bradley, T. Virgili, D.G. Lidzey, and H. Antoniadis, *Appl. Phys. Lett.,* **79,** 3872-3874 (2001).
51. A. Kraft, A.C. Grimsdale, and A.B. Holmes, *Angewandte Chemie International Edition in English,* **37,** 402-428 (1998).
52. U. Mitschke and P. Bauerle, *J. Mater. Chem.* **10,** 1471-1507 (2000).
53. M.Y. Gao, B. Richter, S. Kirstein, and H. Mohwald, *J. Phys. Chem.,* **B102,** 4096-4103 (1998).
54. I. Benjamin, H.P. Hong, Y. Avny, D. Davidov, and R. Neumann, *J. Mater. Chem.,* **8,** 919-924 (1998).
55. H. Hong, D. Davidov, M. Tarabia, H Chayet, I. Benjamin, E.Z. Faraggi, Y. Avny, and R. Neumann, *Synth. Met.,* **85,** 1265-6 (1997).
56. A. Wu and M. Kakimoto, *Adv. Mater.,* **7,** 812-14 (1995).
57. Y. Liu, Q. Li, Y. Xu, X. Jiang, and D. Zhu, *Synth. Met.,* **85,** 1279-80 (1997).
58. D. Braun, and A. J. Heeger, *Appl. Phys. Lett.,* **58,** 1982 (1991).
59. B.S. Chuah, D.H. Hwang, S.T. Kim, S.C. Moratti, A.B. Holmes,

J.C. De Mello, and R.H. Friend, *Synth. Met.*, **91**, 279-82 (1997).

60. D.H. Hwang, S.T. Kim, H.K. Shim, A.B. Holmes, S.C. Moratti, and R.H. Friend, *Chem. Commun.*, 2241-2242 (1996).
61. G. Grem, G. Leditzky, B. Ullrich, and G. Leising, *Adv. Mater.*, **4**, 36 (1992).
62. M. Fukuda, K. Sawaka, and K. Yoshino, *Jpn. J. Appl. Phys.*, **28**, L1433 (1989).
63. M. Fukuda, K. Sawaka, S. Morita, and K. Yoshino, *Synth. Met.*, **41**, 855 (1991).
64. Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Jpn. J. Appl. Phys.*, **30**, L1941 (1991).
65. M. Fukuda, K. Sawaka, and K. Yoshino, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2465 (1993).
66. M. Grell, D.D.C. Bradley, M. Inbasekaran, and E.P. Woo, *Adv. Mater.*, **9**, 798 (1997).
67. M. Kreyenschmidt, G. Klaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W.D. Chen, V.Y. Lee, J.C. Scott, and R.D. Miller, *Macromolecules*, **31**, 1099-1103 (1998).
68. G. Klarner, M.H. Davey, W.D. Chen, J.C. Scott, and R.D. Miller, *Adv. Mater.*, **10**, 993-7 (1998).
69. M. Ranger, D. Rondeau, and M. Leclerc, *Macromolecules* **30**, 7686-7691 (1997).
70. V.N. Bliznyuk, S.A. Carter, J.C. Scott, G. Klarner, R.D. Miller, and D.C. Miller, *Macromolecules*, **32**, 361-369 (1999).
71. Y. He, S. Gong, R. Hattori, and J. Kanicki, *Appl. Phys. Lett.*, **74**, 2265-2267 (1999).
72. I.S. Millard, *Synth. Met.*, **111-112**, 119-23 (2000).
73. M. Leclerc, *Journal of Polymer Science Part a Polymer Chemistry*, **39**, 2867-2873 (2001).
74. N.S. Cho, D.H. Hwang, J.K. Lee, B.J. Jung, and H.K. Shim, *Macromolecules*, **35**, 1224-1228 (2002).
75. K.H. Weinfurtner, H. Fujikawa, S. Tokito, and Y. Taga, *Appl. Phys. Lett.*, **76**, 2502-2504 (2000).
76. C.J. Xia and R.C. Advincula, *Macromolecules*, **34**, 5854-5859 (2001).
77. B. Liu, W.L. Yu, Y.H. Lai, and W. Huang, *Chem, Mater.*, **13**, 1984-1991 (2001).
78. A. Donat-Bouillud, I. Lévesque, Y. Tao, M. D'Iorio, S. Beaupre, P. Blondin, M. Ranger, J. Bouchard, and M. Leclerc, *Chem. Mater.*, **12**, 1931-1936 (2000).
79. I. Levesque, A. Donat-Bouillud, Y. Tao, M. D'Iorio, S. Beaupre, P. Blondin, M. Ranger, J. Bouchard, and M. Leclerc, *Synth. Met.*, **122**, 79-81 (2001).
80. N. Drolet, S. Beaupre, J.F. Morin, Y. Tao, and M. Leclerc, *Journal of Optics a Pure and Applied Optics*, **4**, S252-S257 (2002).
81. J.F. Ding, Y. Tao, M. Day, J. Roovers, and I.-M.D, *Journal of Optics a Pure and Applied Optics*, **4**, S267-S272 (2002).
82. *Dye Laser*, Vol. **1**, edited by F. P. Schafer (1973).
83. E.G. Brock, P. Csavinszky, E. Hormats, H.C. Nedderman, D. Stirpe, and F. Unterleitner, *J. Chem. Phys.*, **35**, 759 (1961).
84. B.H. Soffer and B.B. McFarland, *Appl. Phys. Lett.*, **10**, 266 (1967).
85. H. Kogelnik and C.V. Shank, *Appl. Phys. Lett.*, **18**, 152 (1971).
86. N. Karl, *Physica Status Solidi, A* **13**, 651 (1972).
87. V.G. Kozlov, V. Bulovic, P.E. Burrows, and S.R. Forrest, *Nature*, **389**, 362-4 (1997).
88. M. Berggren, A. Dodabalapur, and R.E. Slusher, *Appl. Phys. Lett.*, **71**, 2230-2232 (1997).
89. M. Berggren, A. Dodabalapur, R.E. Slusher, and Z. Bao, *Synth. Met.*, **91**, 65-8 (1997).
90. F. Hide, M.A. DiazGarcia, B.J. Schwartz, M.R. Andersson, Q.B. Pei, and A.J. Heeger, *Science*, **273**, 1833-1836 (1996).
91. D. Moses, *Appl. Phys. Lett.*, **60**, 3215 (1992).
92. F. Hide, B.J. Schwartz, M.A. DiazGarcia, and A.J. Heeger, *Chem. Phys. Lett.*, **256**, 424-430 (1996).
93. S.V. Frolov, M. Ozaki, W. Gellermann, Z.V. Vardeny, and K. Yoshino, *Jpn. J. Appl. Phys.*, **35**, L1371 (1996).
94. S.V. Frolov, W. Gellermann, M. Ozaki, K. Yoshino, and Z.V. Vardeny, *Phys. Rev. Lett.*, **78**, 729 (1997).
95. N. Tessler, G.J. Denton, and R.H. Friend, *Nature*, **382**, 695 (1996).
96. D.G. Lidzey, D.D.C. Bradley, S.F. Alvarado, and P.F. Seidler, *Nature*, **386**, 135-135 (1997).
97. N. Tessler, N.T. Harrison, and R.H. Friend, *Adv. Mater.*, **10**, 64-8 (1998).
98. A. Schulzgen, C. Spiegelberg, M.M. Morrell, S.B. Mendes, B. Kippelen, N. Peyghambarian, M.F. Nabor, E.A. Mash, and P.M. Allemand, *Appl. Phys. Lett.*, **72**, 269 (1998).
99. T. Granlund, M. Theander, M. Berggren, M.R. Andersson, A. Ruseckas, V. Sundstrom, G. Bjork, M. Granstorm, and O. Inganas, *Chem. Phys. Lett.*, **288**, 879 (1998).
100. A. Dodabalapur, M. Berggren, R.E. Slusher, Z. Bao, A. Timko, P. Schiortino, E. Laskowski, H.E. Katz, and O. Nalamasu, *IEEE Journal of Selected Topics in Quantum Electronics*, **4**, 67-74 (1998).
101. M.D. McGehee, D. Vacar, U. Lemmer, D. Moses, and A.J. Heeger, *Synth. Met.*, **85**, 1233-4 (1997).
102. C. Kallinger, M. Hilmer, A. Haugeneder, M. Perner, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, K. Mullen, A. Gombert, and V. Wittwer, *Adv. Mater.*, **10**, 920-3 (1998).
103. N. Tessler, G.J. Denton, and R.H. Friend, *Nature*, **382**, 695-697 (1996).