

## Conjugated polymers. New materials for optoelectronic devices\*

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*Abstract:* Conjugated polymers now provide a class of processible, film-forming semiconductors and metals. We have worked on the development of the semiconductor physics of these materials by using them as the active components in a range of semiconductor devices. Polymer light-emitting diodes show particular promise, and recent developments in color range (red, green, and blue), efficiency (above 20 lumen/W for green emitters), and operating lifetime are discussed. Progress on their application to displays, with integration with active-matrix TFT drive, and with patterned deposition using inkjet printing techniques is also reviewed. The role played by interfaces between electrode and semiconducting polymer is also discussed.

### INTRODUCTION

Since the first report of metallic conductivities in “doped” polyacetylene in 1977 [1] the science of electrically conducting polymers has advanced very rapidly. More recently, as high-purity polymers have become available, a range of semiconductor devices have been investigated; these include transistors [2–5], photodiodes [6,7], and light-emitting diodes (LEDs) [8–10]. The potential for commercialization is perceived to be high for these semiconductor devices because they are seen to compete in application areas where the market can bear the costs of development. In particular, polymer LEDs now show attractive device characteristics, including efficient light generation, and there are several development programs now set up to establish procedures for manufacture. The principal interest in the use of polymers lies in the scope for low-cost manufacturing, using solution-processing of film-forming polymers.

In parallel with these development activities, much progress has been made in the understanding of the underlying science that controls the properties of these devices. In comparison with inorganic semiconductors, relatively little is known about the electronic properties of these materials; even the nature of the semiconductor excitations remains controversial. There has been considerable progress made recently in resolving some of those issues that determine the limits to device performance, and there have been several recent reviews [11–13]. In this paper, I review progress that has been made in the use of conjugated polymers in LEDs and in photovoltaic diodes.

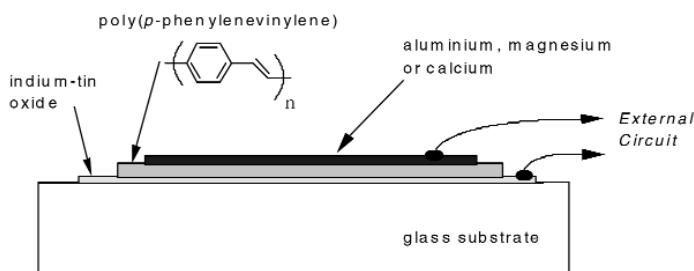
### ELECTROLUMINESCENCE

#### Operation of polymer light-emitting diodes

Conjugated polymers derive their semiconducting properties from having delocalized  $\pi$ -electron bonding along the polymer chain. The  $\pi$  bonding and  $\pi^*$  antibonding orbitals form delocalized valence and conduction wavefunctions, which support mobile charge carriers. Electroluminescence from conjugated polymers was first reported [8] using poly(phenylene vinylene) (PPV), as the single semiconductor layer between metallic electrodes, as is illustrated in Fig. 1.

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\*Lecture presented at the XVIII<sup>th</sup> IUPAC Symposium on Photochemistry, Dresden, Germany, 22–27 July 2000. Other presentations are published in this issue, pp. 395–548.



**Fig. 1** Structure of a polymer LED fabricated with poly(phenylenevinylene) (PPV), as the active semiconductor.

In this structure, the indium-tin oxide (ITO) layer functions as a transparent electrode and allows the light generated within the diode to leave the device. The top electrode is conveniently formed by thermal evaporation of a metal. LED operation is achieved when the diode is biased sufficiently to achieve injection of positive and negative charge carriers from opposite electrodes. Capture of oppositely charged carriers within the region of the polymer layer can then result in photon emission.

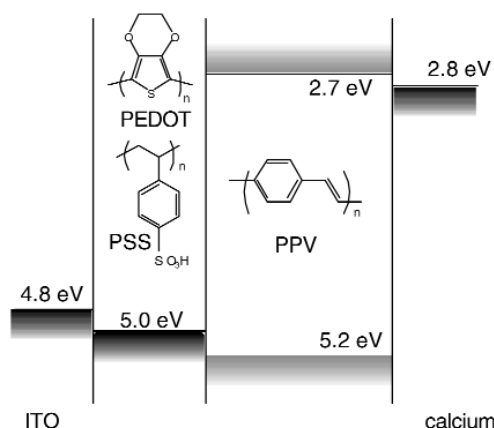
Diodes of this type can be readily fabricated by solution-processing the semiconducting polymer onto the ITO-coated glass, even though the film thickness is no more than typically 100 nm. Spin-coating from solution has been demonstrated to be capable of producing highly uniform layer thickness, with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

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

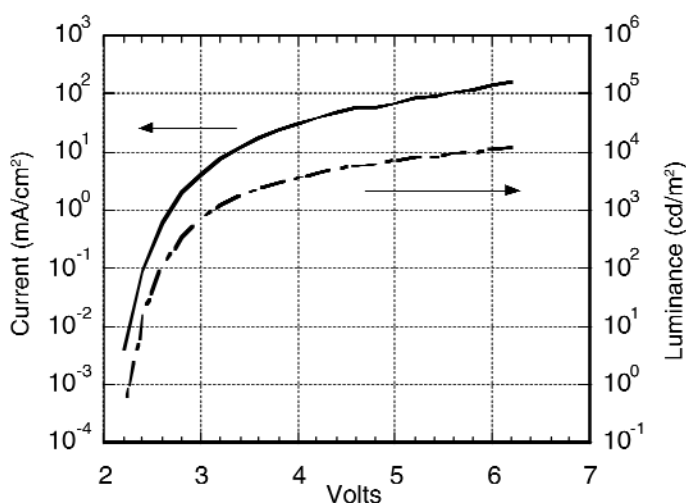
The levels of efficiency of the first, simple LEDs based on PPV, which were fabricated with aluminum negative electrodes, were relatively low, of order 0.01% photon generated within the device per electron injected. These values have risen rapidly over the past five years as improved understanding of the operation of these devices, aided in considerable measure by parallel developments made with sublimed molecular film devices [14], has allowed considerable optimization of the device characteristics. More recently, very much higher efficiencies have been reported for diodes made with similar structures to that shown in Fig. 1, but with a layer of poly(dioxyethylene thienylene) doped with polystyrene sulphonic acid (see Fig. 2) between ITO and emissive polymer layers. Efficiencies in the green part of the spectrum up to 22 lumen/W for emissive polymers based on polyfluorene [12]. Current-voltage-luminescence characteristics for these polyfluorene-based devices are shown in Fig. 3. Such devices are well matched to drive from standard silicon circuits, showing typical display brightness (100 cd/m<sup>2</sup>) below 3 V.

There has been very considerable progress made with chemical modification of conjugated polymers to tune color of emission so that full-color displays can be fabricated. Blue emission is achieved in a wide range of polymers, including the poly(fluorene)s (see, e.g., [15]), and red-emitting polymers have been developed by the Dow Chemical Company and others. In general, blue-emitting materials suffer from the tendency to form aggregate states which show red-shifted emission, and it is generally found that this effect is enhanced for electroluminescence in comparison with photoluminescence.

There is much interest in understanding what determines the limit to LED efficiency. The internal quantum efficiency,  $\eta_{\text{internal}}$ , is usually expressed as the product of the efficiency of electron-hole capture within the semiconductor layers,  $\gamma$ , the fraction of excitons produced as singlets (rather than



**Fig. 2** Schematic diagram of the energy levels for a polymer LED formed with a layer of the conducting polymer system PEDOT-PSS, which acts as hole-injecting electrode, formed on glass coated with indium-tin oxide (ITO). The cathode is formed with vacuum-sublimed calcium. The figure shows energies for the metal work-functions, and for the ionization potential and electron affinity for the semiconducting polymer.



**Fig. 3** Current and light output versus drive voltage for green-emitting polymer LEDs based on polyfluorene [12]. These diodes show turn-on for current and light near 2 V applied bias, and reach 100 cd/m<sup>2</sup> at 2.6 V, and 1000 cd/m<sup>2</sup> at 3.1 V. Peak efficiencies of 22 lumen/W are achieved near 100 cd/m<sup>2</sup>.

triplets),  $r_{st}$ , and the fraction of singlet excitons which decay radiatively,  $q$ , (which is often set equal to the photoluminescence quantum efficiency),  $\eta_{\text{internal}} = \gamma r_{st} q$ .

The process of double-charge injection, the requirement to balance electron and hole currents, and the requirement to achieve electron-hole recombination within the active semiconductor layer (and appropriately spaced away from the electrodes) has proved to be more tractable to engineering of electrodes and semiconducting polymers than was earlier considered feasible, and it seems that the value of  $\gamma$  is close to 100% for the better-performing devices now made. As discussed below, one important approach is to construct heterostructure architectures, with two polymers used to transport either electrons or holes, with recombination forced to occur close to the heterojunction [10]. There has also been much work on the improvement of the process of charge injection at the two electrodes, and devices

which retain the simple single-semiconductor-layer architecture can also show very high efficiencies [16]. One approach to this is to arrange that the barrier for hole injection, which is shown as a single discontinuous step in Fig. 2, is formed by a graded-composition of self-assembled polymer bilayers, so that the barrier for injection takes the form of a series of smaller steps [16].

Radiative decay rates for singlet excitons in semiconducting polymers are now relatively high in many of the materials used in LEDs, often above 50% [12]. Though this is now well accepted, there had been considerable concern that intermolecular interactions would lead to solid-state quenching (through, for example, formation of Davydov-split intermolecular excitons), and the reasons why this is not found for the polymers are being investigated, see e.g., [17].

The third term that enters the expression for the internal quantum efficiency is the fraction of excitons that form as emissive singlet excitons. It had generally been assumed that this would be set by spin statistics, with 25% of electron-hole pairs forming singlets, and 75% forming triplets. Given that the exchange energy for these materials is large ( $>0.5$  eV), intersystem crossing is unimportant, so this would limit device efficiency to 25% of the product of  $\gamma$  and  $q$ . However, experiments now show that this value can be considerably higher, of order 45% [16,18], and there is considerable interest in identifying possible models for spin-dependent electron-hole recombination [19].

The external quantum efficiency depends on the out-coupling light generated in the device in the forward direction, and is modeled and measured for devices that are made as described above to be as high as  $1.2/n^2$  where  $n$  is the substrate refractive index (this is the case when the radiative dipole moments lie parallel to the plane of the device, as is found for many of the spin-coated polymer semiconductors) [20].

## Polymer displays

The obvious attraction of these solution-processed polymer LEDs is that they can be coated over large areas, so that arrays of devices can be conveniently assembled. Passive-matrix addressing provides a particularly convenient arrangement for assembling a display. For this, the bottom electrode (ITO) is arranged as a series of columns, the polymer layers are deposited by spin-coating and do not require lateral patterning (since cross-talk via these polymer layers can be arranged to be unimportant), and the cathode electrode is arranged as a series of rows. Addressing is done by powering each row in sequence, while holding the column voltages as required. The rectifying characteristics of these diodes remove cross-talk and give good performance for displays with no more than “intermediate” information content, e.g.,  $1/4$  VGA ( $320 \times 240$  pixels).

Beyond this, the need to drive each row for shorter times to higher peak currents becomes limiting, and there is now interest in using the active-matrix schemes used for high-quality liquid crystal displays (LCDs). These use amorphous silicon thin-film transistor circuits to provide a latch circuit at each pixel, which maintains the correct potential at the liquid crystal cell throughout the refresh cycle. To extend this drive scheme to the organic LEDs requires that the transistor circuit be able to drive current through the LED, and this is not easily accomplished with amorphous silicon transistors because carrier mobilities are low. However, amorphous silicon can be re-crystallized *in situ*, particularly by laser-annealing, to form poly-crystalline silicon, and this shows much improved mobilities for the field-effect charges, and hence improved speed and current-carrying capacity. This has been developed for the LCD displays in order to allow the address decoding to be performed by circuitry on the glass substrate, but turns out to be well-matched for the polymer LEDs [21].

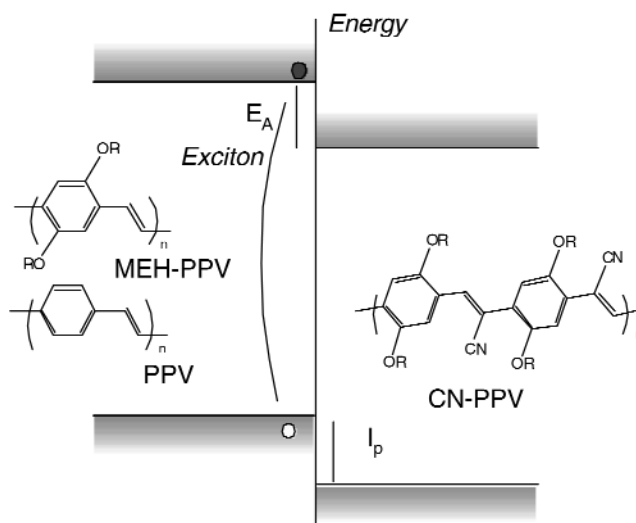
The final step in producing a full-color display is the patterning of red, green, and blue pixels onto such an active-matrix array. One particularly attractive approach is to print the three polymer systems required for each color directly in place onto the back plane, and in this way, avoid the need to employ photolithographic processes. Inkjet printing is particularly suitable for this, and is now demonstrated [21].

## HETEROJUNCTIONS

The use of heterojunctions formed between dissimilar semiconducting polymers has proved to be very powerful, both in applications for LEDs and also for photovoltaic devices. A schematic view of such a heterojunction is shown in Fig. 4. In this scheme, two polymers with similar energy gaps differ in their electronegativities, with CN-PPV selected as a high electron-affinity material, and the two PPVs selected as low ionization potential materials. The offset in band-edge positions is about 0.5 eV for these systems (larger for the dialkoxy-PPV, MEH-PPV, than for the unsubstituted PPV).

The energetics of charges and of excitons in the vicinity of such a heterojunction have been modeled by the Mons group and compared with experiments on model junctions of the type shown in Fig. 4 [22]. What is found is that when the band-edge offsets are larger than the binding energy of the intrachain singlet exciton, such an exciton is ionized, to place the electron on the CN-PPV and the hole on the PPV. This then gives useful photovoltaic operation, particularly when the two polymers are mixed together, to form a large surface area heterojunction device. This is achieved between CN-PPV as shown in Fig. 4 and the dialkoxy-substituted PPV, MEH-PPV [7]. Efficiencies of such devices have been raised to relatively high values, with quantum efficiencies toward 30% and energy conversion efficiencies of order 2% in AM 1.5 conditions [6,23].

In contrast, when the band-edge offset is smaller than the singlet exciton binding energy, the exciton is still stable at the heterojunction (though it will move to the lower-energy-gap side of the junction), and there is little charge generation. This is the case for the heterojunction formed between PPV without the dialkoxy substitution and CN-PPV, and such structures are very effective for use in LEDs, in which electrons and holes are transported from either side of the device, and are trapped at the heterojunction, allowing very efficient electron-hole capture [10].



**Fig. 4** Schematic representation of a heterojunction formed between two semiconducting polymers. As discussed in the text, the offset in band-edge position is sufficient to cause exciton ionization in the case of MEH-PPV versus CN-PPV, so that photovoltaic operation is achieved, whereas for the junction formed between PPV and CN-PPV, exciton energy transfer to the lower-gap material, CN-PPV, occurs.

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