

1. Title of the project

Polymer light-emitting diodes with doped charge transport layers

2. Applicants

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5. Abstract

Polymer light-emitting diodes (PLEDs) become more and more popular in commercial applications because of its potential of cheap fabrication and high efficiency. Multilayer PLEDs involving an electron transport layer (ETL), a hole transport layer (HTL) and an emission layer (EL) are advantageous for their charge balance and controllable position of the emission zone. Compared with single layer devices, the thick layer stack (around 500 nm) of multilayer LEDs reduce the risk of short-circuits and are therefore suitable for large-area implementations. However the high potential drop over the transport layers limits this method for display technology. This work proposes a scheme based on the molecular doping approach. Using this technique even an organic p-n homojunction can be achieved by doping the same host matrix with both n- and p- type dopants. The operation voltage can be largely reduced by the doping effect. With further refined doping techniques PLEDs will become more competitive in the future.

6. Duration of the project

4 years, starting from September 2007.

7. Personal

7.1 Senior-scientists

Name	Task in project	Time
Prof. Dr. Ir. P.W.M. Blom	Supervision and management	5%
Dr. B. de Boer	Supervision and analysis	10%

7.2 Junior-scientists and technicians

Name	Task in project	Time
Msc M. Lu	Experiments and analysis	100%
J. Harkema	Technical support	10%
F. van der Horst	Technical support	10%

8. Cost-estimates

8.1 Personnel positions

One 'onderzoeker in opleiding' position for four years.

8.2 Running budget

15 k€/ year

8.3 Equipments

Equipments	Price (k€)
Electrometer Keithley 6514	5
Source meter Keithley 2400	5.5
PC+IEEE interface	1.5
Sample holder (home-built)	4
TOTAL	16

8.4 Other support

The project is part of a larger research program of the Zernike Institute for Advanced Materials. Involved personnel as described above is employed via the Zernike Institute for Advanced Materials or associated research programs.

8.5 Budget summary (in k€)

	2007	2008	2009	2010	2011	TOTAL
Personnel (positions)						
PhD students	17	43	43	43	26	172
Postdocs	-	-	-	-	-	-
Technicians	-	-	-	-	-	-
Guests	-	-	-	-	-	-
Personnel (costs)	17	43	43	43	26	172
Running budget	6	15	15	15	9	60
Equipment FOM-part	16	-	-	-	-	16
TOTAL	39	58	58	58	35	248

9. Introduction

Conjugated Polymers (CPs) have gained considerable attention in the past few decades since their semiconducting properties were discovered. The main advantage of CPs is that the π -electrons can be excited while the σ -bonds backbone still remains intact. One well-known organic semiconductor is the polyacetylene, which has alternating single and double bonds between carbon atoms [Fig. 1]. Conjugated polymers can be converted to conductors through doping.

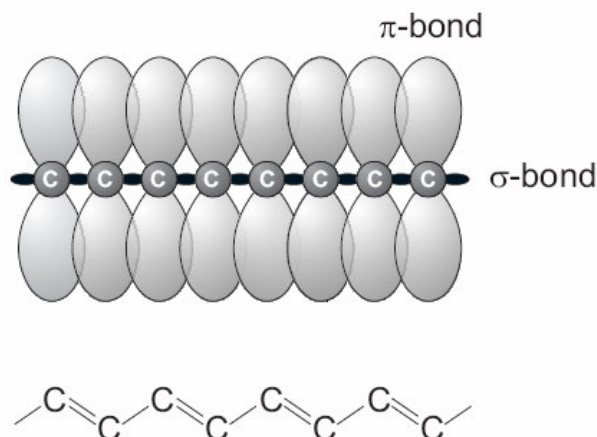


Figure 1. Chemical structure and schematic drawing of polyacetylene.

Polymers sandwiched between two suitable metal electrodes have shown potential for lighting applications. Under forward bias, electrons are injected from a low work function cathode and holes are injected from a high work function anode. Both of them will be released by the local distortion of the conjugation and create polarons. Charge carriers hop from one conjugated segment to another and lead to a net current. Positive and negative polarons can form Frenkel excitons with a high binding energy of 0.2-0.5 eV, compared to the Wannier excitons formed in inorganic material of around 4 meV. The recombination of electrons and holes releases energy in the form of light.

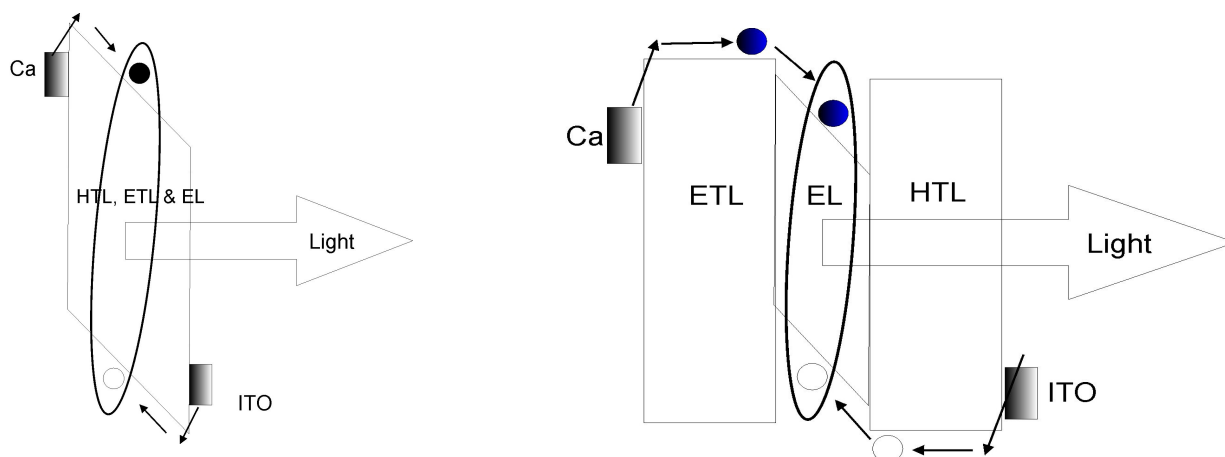


Figure 2. Energy-band diagram and working principle of a single-layer PLED (left) and a trilayer PLED (right).

In a single layer device [Fig. 2 left] the polymer layer has to perform three functions at the same time: efficient electron transport, efficient hole transport and high efficiency of emission (or recombination). To achieve a high efficiency, devices have to be fabricated with layer thicknesses of ~80-100 nm to compensate for the poor charge (both electrons and holes) transport (conductivities) of the polymers. Such a thin active layer limits this technique in large-area applications, since for high-throughput processing, such as inkjet printing or roll-to-roll production, it is difficult to get a uniform layer with a thickness of 80 nm. The risk of short-circuits will be very high, and moreover, an inhomogeneous active layer is unsuitable for lighting applications. Currently, large-area applications suffer from the fact that the layer thickness is not uniform enough to have a homogeneous electric field and, consequently, a uniform emission from the total area.

To solve these problems, the proposed work is focused on trilayer devices with a hole transport layer (HTL, having high conductivity for holes through p-type doping), an electron transport layer (ETL, having high conductivity for electrons through n-type doping) and an emission layer (EL, having high electroluminescence quantum efficiency). In an ideal trilayer PLED the doped transport layers have high conductivities, and thus almost no band bending will occur for these two layers on the energy diagram [Fig. 2 right]. The potential drop will therefore be concentrated on the emission layer. The HTL and ETL are designed as electron and hole blocking layer, respectively, to confine the charges in the emission layer (EL), and thus improve the device efficiency.

One complication of trilayer devices is the solubility issue: the solvent used for processing the consecutive layer should not damage the existing layer. There are several methods to tune the solubility of the polymer: (i) Add certain functional groups to the polymer. (ii) Change the length of the side-chains of the polymer. (iii) Add special co-solvent to the solution. The experiment will be designed as following:

- The first layer (HTL) will be a F₄-TCNQ doped PPV derivative which has very short side-chains and is not soluble in toluene ^[1]. The two materials will be dissolved in chloroform or chlorobenzene and mixed with a certain ratio. Charge transfer between host and dopant may occur in the solution and the polymer host might start to aggregate. In that case polar aprotic co-solvent (DMSO or DMF) has to be added into the solution to prevent the aggregation of the polymer.

- The second layer (EL) will be the undoped NRS-PPV (or super yellow-PPV), a highly emissive polymer. The solvent for the solution will be toluene, so the spin-coating of the second layer will not destroy the first layer.
- The design of the third layer (ETL) is the most difficult part in the research. One choice would be polyfluorenes doped with ionic salts (for instance, Cs_2CO_3). Another choice is $\text{F}_4\text{-TCNQ}$ doped with pentacene or a certain PPV derivative. The solvents for the materials still need to be figured out. We are trying to use methanol or ethanol, since these solvents do not dissolve NRS-PPV. However, polyfluorene or $\text{F}_4\text{-TCNQ}$ also does not dissolve in methanol or ethanol. Probably a special co-solvent will be used in this step.

It is also possible to dope small organic molecules as has been proven successfully by Leo *et. al* ^[2]. However, small-molecule OLED technology requires vacuum deposition and this makes the production process more expensive. This research will concentrate on doping of polymers and their application by spin coating.

10. Description of the research

10.1 p-type and n-type doping

For p-type doping, the lowest unoccupied molecular orbital (LUMO) of the dopant needs to match the highest occupied molecular orbital (HOMO) of the host [Fig. 3 left]. Organic materials like $\text{F}_4\text{-TCNQ}$, TCNQ, DDQ and C_{60} are possible candidates for p-type doping, depending on the host material. $\text{F}_4\text{-TCNQ}$ has a low-lying LUMO of 5.2 eV and has proven to be an effective dopant for small molecule compounds like ZnPc or TDATA. With a doping ratio of 1% $\text{F}_4\text{-TCNQ}$ in ZnPc, the conductivity is observed to be 2 orders higher than nominally undoped ZnPc. A complete charge transfer has been measured by infrared spectroscopy ^[3]. For polymers the technique of doping is still under development. Previous work in our group showed that the output current density can be increased by two orders of magnitude through doping.

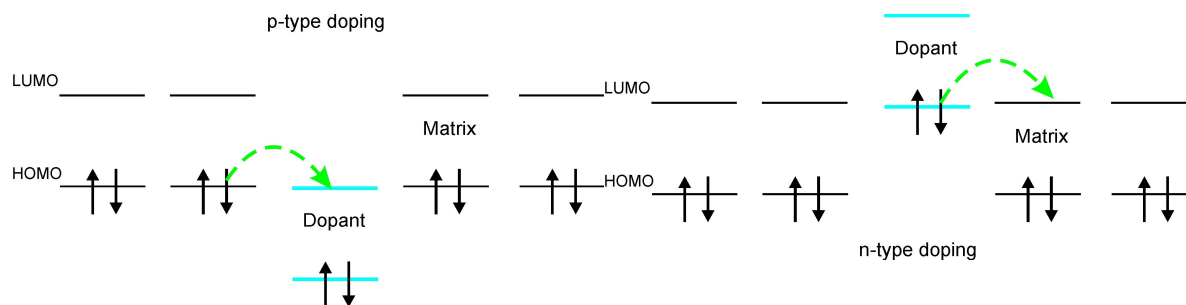


Figure 3. Schematic drawing of p-type (left) and n-type (right) doping mechanism. The molecular dopant acts as acceptor in p-type doping and as donor in n-type doping. The energetic overlap of matrix and dopant energy levels is crucial.

For n-type doping, the HOMO of the dopant needs to match the LUMO of the host [Fig. 3 right]. Up till now n-type doping is still a challenge. Normally there are three different approaches: doping with alkali metals, with organic molecules which have a high-lying HOMO or with cationic salts. The disadvantage for doping the organic matrix with alkaline metals is that the alkaline ions may drift under the applied electrical bias. The proposed work is therefore aimed on the molecular compounds doping or cationic salts doping. While these dopants are usually not air stable and are easily oxidized, the whole procedure has to be carried out under nitrogen protection and in the end the doped layer is encapsulated in an airtight condition.

10.2 Contacts and modeling

Doping can also be used to improve charge injection into the EL of devices. Especially for blue polymers which have a large band gap, it is hard to find proper contact materials with a suitable work function to fit the HOMO or LUMO of the polymer and form ohmic contacts. For inorganic semiconductors, the contact problems are solved through doping. Noble metals are deposited as the electrode. After annealing, part of the metal ions diffuse into the semiconductor and form a highly doped region. A similar procedure also works for organic contacts. The doping effect reduces the width of the space charge region between the metal and polymer and lets charge carriers tunnel through the barrier [Fig. 4]. Generally in LEDs, cathodes are made of high reactive low work function materials and can be damaged by the oxygen or water molecules in the environment. This limits the lifetime of the devices. With doping techniques, even non-reactive high work function

metals can be used as cathode, since the injection barrier is not a problem anymore. As a consequence, the device lifetime can be significantly improved.

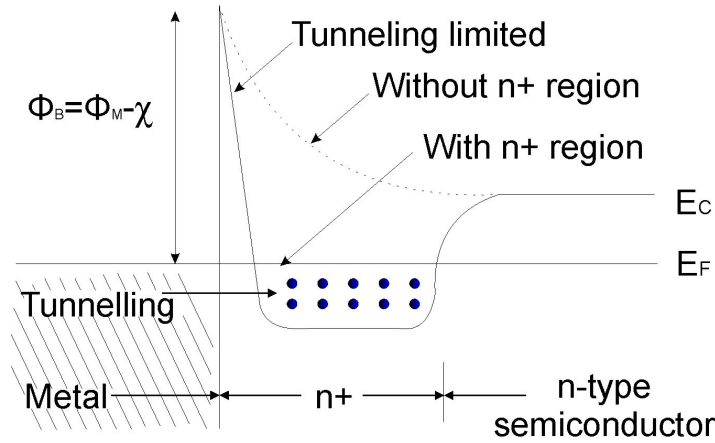


Figure 4. Energy level diagram of an Ohmic contact for electron injection through doping (n-type).

For a polymer device, whether an electron-only (EO), a hole-only (HO) or a light-emitting diode (LED, having both charge carriers), the J - V property deviates from classical Shockley theory when the applied voltage (V) is larger than the built-in voltage (V_{bi}). Generally for single carrier trap-free devices it follows the Mott-Gurney relation ^[4]:

$$J = \frac{9}{8} \epsilon_0 \epsilon_s \mu \frac{V^2}{L^3}$$

where ϵ_0 is the permittivity of vacuum, ϵ_s is the relative dielectric constant of the semiconductor, μ is the carrier mobility and L is the thickness of the device. The J - V property of the devices and the effectiveness of the doping effect will be studied with the following procedure:

- 1) The hole transport properties of undoped polymers are obtained from a density dependent mobility model ^[5]. Under high bias or low temperature, a field and temperature dependent mobility model is involved ^[6].
- 2) By using the same model the hole transport properties of p-type doped polymers with different doping ratio can be studied. Compared with the results from the undoped polymers, the influence of the doping effect will be calculated numerically. The p-type doping concentration p_0 can be checked by the impedance spectroscopy (IS). The degree of the charge transfer from donor to acceptor (Z) can be measured by Fourier transform infrared spectroscopy (FTIR).

- 3) Most of the polymers, such as PPVs, exhibit a trap-limited electron current. In this case electron transport properties of undoped polymers are obtained by using the same parameters as obtained for the holes, while at the same time an exponential trapping model is implemented into the model^[7, 8].
- 4) The properties of n-type doped polymer can be studied in a similar way.
- 5) After both electron and hole transport properties are available, LED data (for both doped and undoped polymers) can be modeled with a double-carrier transport model.

The modeling is an objective and a tool for gaining further insight in the fundamental physics involved, which can be used to optimize and further improve the experimental work.

Other problems that might be encountered in a trilayer device are: charge unbalance, interface exciplexes, and exciton quenching by excess charge carriers, which limit the device efficiency. To solve this, the HTL (ETL) will also be designed as an electron (hole) blocking layer instead of using a five-layer structure (ETL, HBL, EL, EBL, HTL), to avoid extra processing steps.

10.3 Goals of the project

The goals of the project are:

1. work out effective ways for both p-type and n-type doping of polymers, and find the optimized doping ratio for thick transport layers (around 200 nm).
2. solve the solubility issue and figure out the appropriate solvents for each polymer layer processing.
3. make stable working trilayer LEDs: long life time, transmitting uniform light with a high power efficiency.
4. obtain all parameter of the device from the modeling and fully study the doping effects on charge transport and electroluminescence properties.

11. Targets and deliverables

- First year:

The proposed work starts with a p-type doped HTL — a PPV derivative with very short side-chains doped with F₄-TCNQ. The whole layer is spin-coated from chlorobenzene or chloroform solution. DMSO or DMF will be added to the solution to prevent the aggregation. The effect of doping on the hole transport properties will be

studied by using the density dependent mobility model^[5]. PEDOT:PSS are commonly used as a hole injection layer (HIL) in organic semiconductors. ITO is usually used in LEDs as transparent anode.

- Second year:

Bilayer devices with a HTL and an EL will be fabricated [Fig. 5]. On top of the HTL, the EL, NRS-PPV, will be spin-coated from a toluene solution. Part of the research will be focused on the optimization of the thickness of the EL. On one hand, if the EL is too thin, the HTL will touch the ETL leading to extra percolation paths. On the other hand, if the EL is too thick, the large device resistance will cost more energy. All the potential should drop across the EL and the field (V/d) will determine how effective this is. The starting thickness for the EL will be 80 nm. The dopant diffusion and exciton quenching effects will be studied.

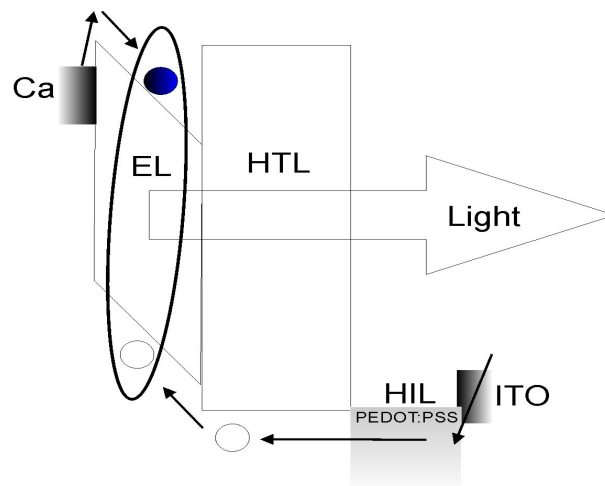


Figure 5. Energy-band diagram of a bilayer architecture PLED with PEDOT:PSS acts as HIL.

- Third year:

A n-type doped ETL layer will be designed. The first try will be polyfluorenes doped with or F₄-TCNQ doped with an organic polymer. Again, the spin-coating of the ETL should not destroy the previous layers (EL and HTL). Efficient doping methods and proper solvents for the solution will be figured out.

- Forth year:

The complete trilayer structure PLEDs will be evaluated. The project will be summarized into a Ph.D. thesis.

12. Infrastructure

The Molecular Electronics group has a variety of processing and measuring facilities. For this project the most relevant equipments are:

- Reactive and noble metal deposition system
- Spin coater glove box
- Wet station
- Kelvin probe
- Luminance meter LS-110
- OceanOptics USB 2000 spectrometer
- Atomic force microscope (AFM)
- Ellipsometer
- Dektak 6M STYLUS PROFILER
- Keithley 2400 source meter

All these equipments are not included in this proposal and will be financed by other means. Additionally, all facilities and equipments of the Zernike Institute for Advanced Materials will be available for use.

13. Application perspective in industry, other disciplines or society

Polymeric semiconductors are promising candidates for substituting inorganic semiconductors for a number of applications because of their ease of processing and therefore potential low cost production. Polymer materials can be used for fabricating flexible large-area light source like pixel display or flat panel display. PLEDs have a faster response time and enable a larger viewing angle than LCDs, because PLED pixels emit light directly. Nowadays, PLEDs have already been used in mobile phones, MP3 players *etc.* The proposed work is based on a more robust and thicker device architecture, which is especially suitable for industrial processing techniques such as inkjet printing, screen printing or roll-to-roll production. The thick polymer layer makes the roughness of ITO less important, so processing on low cost unpolished ITO substrates becomes possible. Furthermore, large-area applications become feasible, since layer thickness variation is less crucial when using multilayer LEDs. With further improving life time and power efficiency, PLEDs will have a tremendous future.

Reference

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