Semiconducting Polymer Matrix as Charge Transport Materials and its Application in Polymer Electronic Devices

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Abstract

In the last decade, a number of intensive studies have been conducted to achieve efficient polymer light-emitting diodes (PLEDs). As a result of extensive multidisciplinary efforts, modern PLEDs offer substantial benefits over conventional cathode ray tubes (CRT) and liquid crystal displays (LCD). PLEDs display provides superior brightness and color purity, markedly lower power consumption, as well as full viewing angle without compromising image quality. Compared with small molecule organic LEDs (OLEDs), PLEDs use solution-based processes, which offer the potential for lower cost and roll-to roll processing on flexible substrates.

An efficient PLED device typically consists of a stack of organic/polymeric thin layers, each of which performs a specific function aimed at improving the device performance or achieving the desired device functionality. In many cases, these layered structures are formed from the polymeric solution by spin-casting or printing with subsequent removal of the solvent carrier. However, solvent from the freshly deposited film frequently dissolve or partially dissolve the underlying layer, resulting in loss of the desired structure and corresponding device functionality. Undesirable changes in the morphology and interfaces of the polymer films are another detrimental effect associated with incompatible solvent and its removal.

To make more robust hole transport layers (HTLs) and avoid solvent damage from subsequent emissive layer, the most common approach is to introduce polymerizable functional groups onto the base structure of the molecules with hole transporting (HT) property to form a cross-linkable HT molecules, which can form a cross-linked HTL upon treatment. However, such a type of polymerizable hole transport material is expensive and difficult to make, especially in large quantity.

Herein we report a new approach to address this issue: Commercially available HT polymers are embedded into a cross-linked polymer network to "lock" uniformly distributed HT polymers inside the cross-linked polymer matrix. This approach proves to be more advantageous in terms of process simplicity and cost. Similarly, the same class of materials can potentially be employed in other polymer electronic devices, such as the organic photoconductor.

An organic photoconductor commonly used in electrophotographic applications is a dual layer structure consisting of a thin (0.1um - 2 um) charge generation (CGL) bottom layer and a thick (about 20 um) charge transport (CTL) top layer. Light passes through the transparent CTL and strikes the CGL that generates free electrons and holes. Electrons are collected by the electrical ground of the photoreceptor and holes are driven towards to top of the CTL by an applied electrical field. CTL allows hole transport towards the surface, at which they are used to neutralize negative surface charges deposited during the pre-charging process. In essence, CTL consists of non-conductive organic material (usually polymer) with charge transport moieties embedded into it. We believe this semiconducting polymer matrix can act as charger transport materials for organic photoreceptor.

Introduction

The growth and proliferation of electronic devices has created a significant industry-wide demand for new, low-power, light and low-cost display technologies. This demand underlies a current display development initiative within display industries. In the last decade, a number of intensive studies have been made to achieve efficient polymer light-emitting diodes (PLEDs). Chemistry and chemical principles have played a crucial role in the evolution of efficient PLEDs. As a result of extensive multidisciplinary efforts, modern PLEDs offer substantial benefits over conventional cathode ray tubes (CRT) and liquid crystal display (LCD). PLEDs display provides superior brightness and color purity, markedly lower power consumption, as well as full viewing angle without compromising image quality. Compared with small molecule organic LEDs (OLEDs), PLEDs use solution-based processes, which offer the potential for lower cost and roll-to roll processing on flexible substrates. To realize these favorable advantages, significant chemical and physiochemical challenges must be addressed. These challenges include (i) excellent multilayer solution-processability , (ii) improved efficiency via balanced charge carrier injection and leakage current reduction, (iii) better thermal stability and (iv) increased operational lifetime [1].

An efficient PLED device typically consists of a stack of organic/polymeric thin layers, each one of them performing a specific function aimed at improving the device performance or achieving the desired device functionality. In many cases, these layered structures are formed from the polymer solution by spin-casting or printing with subsequent removal of the solvent. However, solvent from the freshly deposited film frequently dissolve or partially dissolve the underlying layer, resulting in loss of the desired structure and corresponding device functionality. Undesirable changes in the morphology and interfaces of the polymer films are another detrimental effect associated with solvent removal. To make more robust hole transport layers (HTLs) and avoid solvent damage from subsequent emissive layer, the most common approach is to introduce polymerizable functional groups onto the basic structure of the molecules with hole transporting (HT) property to form a cross-linkable HT molecules, which can form a cross-linked HTL upon spin coating [2-8]. However, this type of polymerizable hole transporting material is expensive and difficult to make. Herein we report a new approach to address this issue: Commercially available HT polymers are embedded into a cross-linked polymer network to “lock” uniformly distributed HT polymers inside the cross-linked polymer matrix. This approach proved to be more advantageous in terms of process simplicity and cost.

Results and Discussion

The basic multilayer heterostructure and energy level diagram of PLED is shown in **Figure 1**. Components include a transparent conducting anode, hole injection layer (HIL), HTL, emissive layer (EML), electron-transporting layer (ETL), and metallic low work function cathode. For a convenient demonstration, we have chosen indium tin oxide (ITO) as anode, poly (3,4-ethlyenedixoythiophene)- poly(styrene sulfonic acid (PEDOT-PSS) as hole injection layer, poly(9,9- dioctylfluorene-co-N-(4-butylphenyl)diphenylamine (ADS132GE) as HTL, poly(9.9-dioctylfluorenyl-2,7-diyl) (PFO) as EML and Ba-Al as the cathode (chemical structures shown in **Figure 2**). This set of materials might not be optimum in terms of interfacial energy alignment for the transport of holes and electrons, but suffices for the demonstration of the function of our embedded HTL materials.

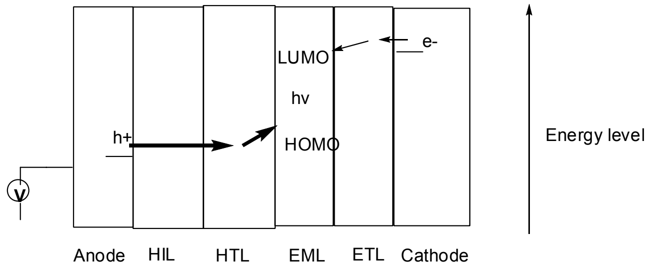

***Figure 1** Schematics of Typical PLED Heterostructure*

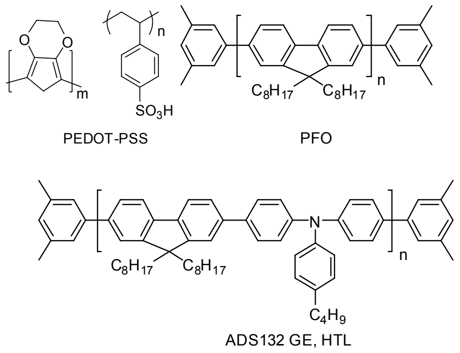

***Figure 2** The structures of HTL, EML and HIL polymers*

In a demonstration device, the HIL, HTL, and EML layers were sequentially spun-cast onto a glass substrate with a pre-patterned ITO anode. A Ba-Al film was then thermally evaporated to form a cathode. As we know, solvents that are used for EML polymers are commonly shared by the under-layer HTL polymer. To minimize the undesirable impact from solvents that are used by the EML polymer, we embed the HTL molecules into the inert cross-linked polymer network. The cross-linkable polymer is selected so that the electrical and electro-optical properties of the embedded polymer are retained. At the same time, the cross-linked polymer network helps maintain the morphology of the embedded organic film during solvent removal. There are many options could be employed to form the cross-linked inert polymer network: a mixture of cross-linkable monomer, oligomers, and polymers, in addition to cross-linking agent and an initiator. The cross-linking agent could be a 2-branch, 3-branch, or 4-branch cross-linker. Cross-linking could be activated using appropriate energy sources such as thermal process or UV-exposure. Some examples of the cross-linkers are 2-branch cross linkers such as ethoxylated (2) bisphenol A dimethylacrylate (EBDA) and 3-branch corsss linker such as trimethylopropanes trimethylacrylates (TPTA) to increase the cross link density (**Figure 3**).

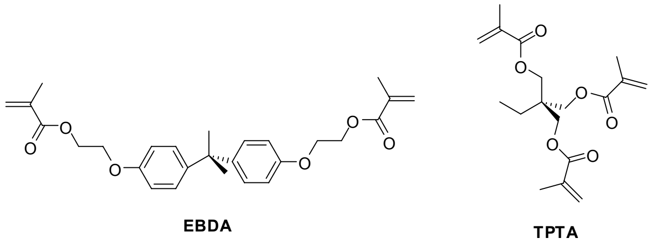

***Figure 3** The structures of cross-linkers EBDA and TPTA*

Two commercial available cross-linking agents, the thermally curable binder ethoxylated bisphenol A dimethacrylate esters (EBAD) and the UV curable binder NOA83H, were investigated for incorporating hole transport material ADS132 into the polymer network to form the HTL. The HTL also acts as an electron blocking layer (EBL). First, the solvent resistibility of the spin-coated films from the mixture solution of ADS132 and cross-linking material were tested by washing the film with chloroform and toluene. In both cases using EBAD and NOA83H, the potoluminescence of the films before and after washing remained the same. No change of film thickness and morphology was found after washing the films with the solvents

Thin films of HTL with and without a supporting cross-linked polymer were fabricated by spin-coating the ADS132GE or a mixture of ADS132GE and EBDA or NOA83H on ITO substrates. These films were tested by washing with toluene and chloroform and subsequently measuring their photoluminescence (PL). For reference, the PL of HTL-only samples was also measured. The results, shown in Figure 2 (right), suggest that the HTL material was mostly washed away when exposed to the solvent used for the EML deposition. On the other hand, the HTL material was mostly retained when using either cross-linking agent. This is verified by corresponding AFM studies that show no change of the film thickness and morphology after the solvent washing.

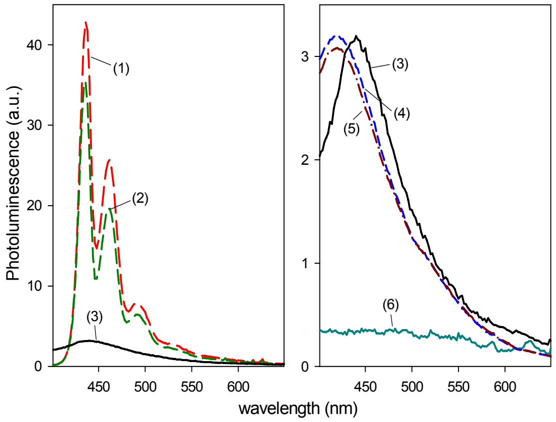

Figure 3 *Photoluminescence of the:* ***(1)*** *HTL/EML film; EML was deposited directly on the HTL embedded into UV cross-linked matrix (similar result was obtained for the thermally cured polymer);* ***(2)*** *EML only;* ***(3)*** *HTL only;* ***(4)*** *HTL embedded into UV cross-linked matrix;* ***(5)*** *case of (4) after washing with toluene (used as a solvent for depositing both the HTL and the EML);* ***(6)*** *case of (3) after washing with toluene.*

Representaive devices and their device characteristics are shown in Figures **4** and **5**. Sample A doesn't have a HTL/EBL, while sample B and sample C have ADS132 embedded in EBAD and NOA83H, respectively, as HTL material. The selected HTL material, ADS132 has a LUMO energy level that provides a barrier to effectively block electrons coming from the cathode. This electron blocking layer (EBL) drastically reduces the leakage current as evidenced by I-V characteristics of Fig 4B & C vs compared with Fig 4A, which tremendously improves external emission efficiency. The UV cured binder NOA83H (for ADS132GE) shows better performance than thermally cured binder EBAD in blocking leakage current (electron blocking) by 100X to 400X (compare Fig 4B & 4C). In addition to the effect of electron blocking from ADS 132, the low current may be also due to the the extremly high resistivity of NOA83H. HTL/EBL that uses the NOA83H binder also has higher luminescent efficiency. For example, when operated at 4 volt, the EL peak intensity of NOA83H (5C) is 1/3 and 1/30 that of PFO only (5A) and EBAD (5B) respectively (Fig. 5), but using only 1/1000 and 1/400 the amount of current respectively (Fig 4). Therefore, the device with HTL in NOA83H has about 330X and 13X more efficiency than PFO only (without HTL/EBL) and HTL in EBAD device, respectively, which results from the large effect from the leakage current reduction. The EL spectrum distortion shown in device B with EBAD binder might be the result of deep penetration of PFO into the porous EBAD layer; Another possible explainnation is that the excitons are generated at different interface compared with PFO only devices so that the emission may come from ADS132. The different dielectric environment from the surrounding (EBAD and ADS132GE) could modify the energy structure of PFO. The enhancement of electroluminescent efficiency is also owing to a more balanced electron and hole injection by introducing a HTL. This result demonstrates the effectiveness on HTL structural protection offered by the cross-linked NOA83H and the preservation of HTL electrical property that was designed for.

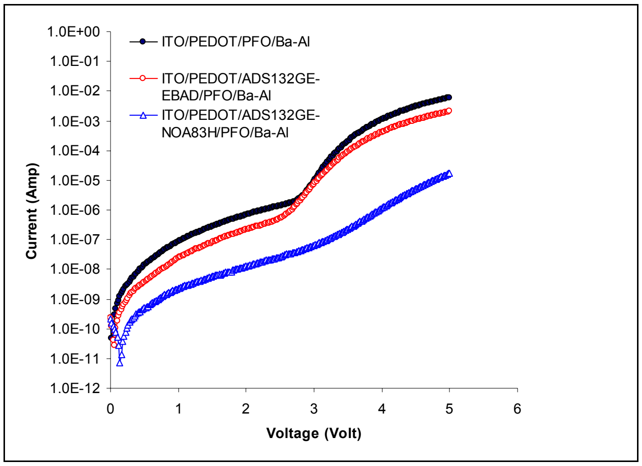

Figure 4 Electrical characteristics of sample structure A:

ITO/PEDOT/PFO/Ba-Al, B: ITO/PEDOT/ADS132GE-EBAD/PFO/Ba-Al, and C: ITO/PEDOT/ADS132GE-NOA83H/PFO/Ba-Al.

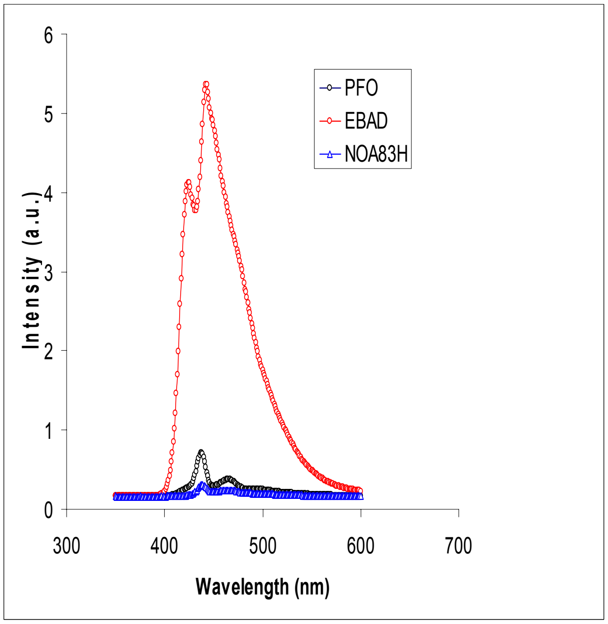

Figure 5 EL intensity and Spectrum of three devices A, B and C at bias voltage of 4 volts.

It is noteworthy that we chose PFO as the emissive layer to prove the feasibility of our concept. Other small organic molecules or polymer light emitting materials, quantum dots (QD) and polymer/QD hybrid emitting devices could be easily used. We are currently developing the polymer/semiconducting nanocrystal hybrid pixel for improved life time, even better color purity and possibly power efficiency.

Table I: Quantum efficiency of device A, B and C at 4V bias. Devices were placed within an integrated sphere to collect all the emitted light

Device	Device structure	Quantum efficiency (%)
A	ITO / PEDOT / PFO / Ba-Al	0.17
B	ITO / PEDOT / HTL-EBDA / PFO / Ba-Al	2.94
C	ITO / PEDOT / HTL- NOA83H / PFO / Ba-Al	8.71

The quantum efficiency of the devices was measured by placing the devices within an integrating sphere so that all the emitted light was collected. **Table 1** compares the quantum efficiencies of the devices measured at 4V. The quantum efficiency for device B and C was 17 times and 50 times that of device A, respectively. The high efficiency of device C is primarily due to the significant reduction in leakage current as compared to devices B and A. A more balanced electron and hole injection also contributed to the enhancement of electroluminescence efficiency when the HTL was added. It is noteworthy that a similar scheme could be used to incorporate emissive species like, for example, semiconducting nanocrystals or their mixtures with the appropriate polymer agents to form a multilayer structure.

An organic photoconductor commonly used in electrophotographic applications is a dual layer structure consisting of a thin (0.1um - 2 um) charge generation (CGL) bottom layer and a thick (about 20 um) charge transport (CTL) top layer. Light passes through the transparent CTL and strikes the CGL that generates free electrons and holes. Electrons are collected by the electrical ground of the photoreceptor and holes are driven towards to top of the CTL by an applied electrical field. CTL allows hole transport towards the surface, at which they are used to neutralize negative surface charges deposited during the pre-charging process. In essence, CTL consists of non-conductive organic material (usually polymer) with charge transport moieties embedded into it. We believe this semiconducting polymer matrix can act as charger transport materials for organic photoreceptor.

Conclusions

We have successfully fabricated multilayer electroluminescent pixels using a process of embedding HTL materials into cross-linkable agents. We have the fine-tuned formulation of cross-linkable monomers to produce uniform thin film layers, which shows good performance in PLED sample devices. The electroluminescence efficiency is enhanced by the more balanced electron and hole injection with this type of HTL. This result demonstrates the effectiveness of the HTL structural protection offered by the cross-linked NOA83H and the desired preservation of HTL electrical properties. This process will be very useful for solution–based multi-layer PLED devices fabrication. We believe this semiconducting polymer matrix can act as charger transport materials for organic photoreceptor.

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