Ph. D thesis

Design and synthesis of full functional block copolymers for electroluminescent application

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Chapter 1. Introduction

1.1. Organic Electroluminescence

1.1.1 History

Electroluminescence (EL) is an optical and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field.

The first observations of EL in organic materials were in the early 1950s by A. Bernanose and co-workers. They applied high-voltage alternating current (AC) fields in air to materials such as acridine orange, either deposited on or dissolved in cellulose or cellophane thin films. [1-4]

In 1960, M. Pope and co-workers at New York University described the necessary energetic requirements (work functions) for hole and electron injecting electrode contacts. [5-7] These contacts are the basis of charge injection in all modern organic light-emitting diode (OLED) devices. Pope's group also first observed direct current (DC) electroluminescence under vacuum on a pure single crystal of anthracene and on anthracene crystals doped with tetracene in 1963. [8]

EL from polymer films was first observed by R. Partridge. The device consisted of a film of poly(N-vinylcarbazole) located between two charge injecting electrodes. The
results of the project were patented in 1975 \[^9\] and published in 1983. \[^{10}\]

The first diode device was reported at Eastman Kodak by Ching W. Tang and Steven Van Slyke in 1987. \[^{11}\] This device used a novel two-layer structure with separate hole transporting and electron transporting layers so that recombination and light emission occurred in the middle of the organic layer. This resulted in a reduction in operating voltage and improvements in efficiency and led to the current era of organic light-emitting diode (OLED) research and device production.

Research into polymeric light-emitting diode (PLED) culminated in 1990 with J. H. Burroughes \textit{et al.} at Cambridge reporting a high efficiency green light-emitting polymer based device using 100 nm thick films of poly(p-phenylene vinylene). \[^{12}\]

1.1.2 Advantages and disadvantages

As emitting materials, polymeric/organic structures possess many advantages over inorganic ones, such as good film-forming properties, susceptible to structure modification and so on. \[^{13-16}\] For example,

- Lower cost in the future;
- Light weight & flexible plastic substrates;
- Wider viewing angles;
- Higher response time; and so on.

However, as a kind of the new birth theory and technology for the commercial
applications, there are unperfected aspects and some ones are difficult of being solved.

- Short lifetime for blue organic EL
- Color balance issues: Blue organic EL materials degrade significantly and rapidly than the other color materials.
- Lower external quantum efficiency of blue organic EL
- Water damage and UV sensitivity

1.1.3 Commercial applications

OLED technology has been recently used in commercial applications such as displays for mobile phones and portable display equipment, car radios and digital cameras, while PLED technology is still in the laboratory research stage.

OLEDs have been used in most Motorola and Samsung color cell phones, as well as some HTC, LG and Sony Ericsson models. Nokia has also recently introduced some OLED products. DuPont stated in a press release in May 2010 that they can produce a 50-inch OLED TV in two minutes with a new printing technology. If this can be scaled up in terms of manufacturing, then the total cost of OLED TVs would be greatly reduced.

1.1.4 EL mechanism

A typical organic EL is composed of a layer of electrically conductive organic
materials situated between two electrodes, the anode and cathode, all deposited on an indium tin oxide (ITO) substrate. Figure 1-1 shows a typical electroluminescent device and its mechanism. During operation, a voltage is applied and a current of electrons flows through the EL device from cathode to anode, as electrons are injected into the lowest unoccupied molecular orbitals (LUMO) of the organic layer at the cathode and withdrawn from the highest occupied molecular orbitals (HOMO) at the anode. This latter process may also be described as the injection of holes into the HOMO. The electron and the hole recombine in the emitting material, forming an exciton, a bound state of the electron and hole. The decay of this excited state results in a relaxation of the energy levels of the electron, accompanied by emission of radiation whose frequency is in the visible region. The frequency of this radiation depends on the band gap of the emitting material, or the energy difference between the HOMO and LUMO. **EL efficiency**, the most important property of EL device, may be expressed as a percentage, is the ratio of luminous/photo flux to power.

![Figure 1-1. (a) Organic EL device and (b) EL mechanism](image-url)
1.1.5 Phosphorescence and fluorescence

An exciton (a bound state of the electron and hole) may either be in a singlet state or a triplet state depending on how the electron and hole have been combined (Figure1-2). Statistically triplet exciton numbers is about three times of singlet exciton numbers. Decay from triplet states (phosphorescence) show a slow decay process (>1ms), while the emission decay from singlet state (fluorescence) takes place over tens of nanoseconds. As a result, the energy trapped in the triplet state returns to the lower energy state, as classically "forbidden" transitions, indicating that the theoretical upper limitation of organic EL efficiency of excitons is 25%.

However, some phosphorescent compounds with heavy metals, such as Ir and Ce, still emit relatively fast, with triplet lifetimes on the order of milliseconds. Hence, this kind of phosphorescent material could be used as dopant to fluorescent polymer to fabricated OLEDs generating light from both triplet and singlet excitons, allowing the internal quantum efficiency of such devices to reach nearly 100%. It is commonly achieved by doping a host molecule with an organometallic phosphorescent complex. [17]
1.2 Polymeric light-emitting diodes (PLEDs)

The first PLEDs based on the electroluminescence of poly(p-phenylenevinylene)(PPV) was reported by Cambridge University’s research group in 1990. From then, PLEDs have attracted great attention due to their potential applications in full-color, large-area, paper-thin flexible displays, and back lighting and so on.

1.2.1 OLED and PLED

In an organic EL device, the organic material is electrically conductive due to the delocalization of π-electrons caused by conjugation over all or part of the molecule, and the material therefore functions as an organic semiconductor. The comparison between devices fabricated with small organic materials (OLED) and polymeric material (PLED) is listed in Table 1-1.
Table 1-1. Comparison between OLED and PLED

<table>
<thead>
<tr>
<th></th>
<th>Organic LED (small-molecules)</th>
<th>Polymeric LED (macro-molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular weight of materials</strong></td>
<td>(1-10)*10^2 g/mol</td>
<td>(1-10)*10^3-5 g/mol</td>
</tr>
<tr>
<td><strong>Material synthesis</strong></td>
<td>Synthesis/purify easily</td>
<td>Difficult, unpurified</td>
</tr>
<tr>
<td><strong>Device fabrication</strong></td>
<td>Evaporation coating (difficult, high cost)</td>
<td>Spin-coating or ink-jet printing (easy, low cost)</td>
</tr>
<tr>
<td><strong>Device characterizations</strong></td>
<td>High EL efficiency, Longer device life time, Color stability, Poor thermal stability</td>
<td>Low EL efficiency, Shorter EL lifetime, Thermal/mechanical stability</td>
</tr>
<tr>
<td><strong>Applications</strong></td>
<td>Commercial manufactured</td>
<td>Laboratory research stage (Large-size display, flexible, low energy-cost)</td>
</tr>
</tbody>
</table>

The molecular weight of organic material is usually about several hundreds, and it is very easy to synthesize and purify. While for the polymeric ones with much larger molecular weight, they need more difficult synthesis route and usually can't be purified.

The device fabrication for OLED is the evaporation coating method, which is a difficult and high cost process; OLEDs show very high performance, such as high EL efficiency, longer device life time, and color stability but the largest problem is poor thermal/device stability. PLEDs can be fabricated by spin-coating or ink-jet printing easily, but they show low EL efficiency and shorter EL lifetime, even they possess good thermal stability and mechanical stability.

The potential advantages of OLEDs include thin, low cost displays with a low driving voltage, wide viewing angle and high contrast and color gamut. PLEDs have
the additional benefit of printable and flexible displays. [20-22] OLEDs have been used to make visual displays for portable electronic devices such as cellphones, digital cameras, and MP3 players while possible future uses include lighting and television while PLED devices are still in the laboratory research stage because of unsatisfactory performance.

1.2.2 The improvement of PLED

The first PLED were reported as single-layer device with PPV inserted between two electrodes simply, emitting yellow-green light, with EL efficiency of only 0.05%. [12] In contrast to the easy fabrication process, the performance of this single-layer PLED (as shown in Figure 1-3. (b)) was typically unsatisfactory due to the high carrier injection barrier, imbalanced carrier injection and recombination zone being close to electrode-emitting layer interfaces. [23]

![Figure 1-3. (a) Single-layer and (b) multi-layer energy organic EL device](image)

[24-25]
To improve device performance, multilayer PLEDs consisting of a hole-transporting layer (HTL), an emitting layer and an electron-transporting layer (ETL), sandwiched between two electrodes, have been designed (Figure 1-3 (b)). Nevertheless, fabrication of the multilayer PLEDs is usually a difficult task, since the emitting layer might be re-dissolved during subsequent spin-coating of the electron injection/transport layer.

Another method is to fabricate PLEDs with dopant/polymer blending systems (Figure 1-4 (a)) instead of the sandwich structure consisting of HTL, emitting layer and ETL. Furthermore the hole-injection layer and electron-injection layer are also inserted to improve the charges injection and transport from electrodes. However the main problem associated with physically blending charge injection/transport molecules, such as oxadiazole, 1,2,4-triazole, triphenylamine or carbazole derivatives, into polymeric hosts is the possibility of phase separation, leading to a lack of long-term device stability. For example, crystallization-induced degradation and thermal breakdown during device operation might readily happen due to their low glass
transition temperature \((T_g)\). \cite{29-31} Therefore, the development of charge injection/transport materials with high \(T_g\) is essential to improve PLEDs’ performance.

Thus, single-layer devices (Figure 1-4 (b)) based on polymer/polymer blend system\cite{32-34} or co-polymers with HTL block and ETL block\cite{35-36} have been considered as a feasible approach to improve this problem, preferred from the viewpoints of process simplicity and cost effectiveness. Several studies have successfully synthesized single polymers containing red-, green- and blue emission units in the backbone of polyfluorene.\cite{37-43}

1.2.3 White LED

White light can be formed by mixing differently colored lights; the most common method is to use individual LEDs that emit three primary colors\cite{44} - red, green, and blue - and then mix all the colors to form white light. Hence the method is called multi-colored white LEDs (sometimes referred to as Red Green Blue LEDs). Blue emitting materials play an important role in enhancing the efficiencies of green-, red-, and white-light-emitting materials because these materials are generally prepared by introducing appropriate doping components into blue-emitting materials. This method is particularly interesting in many uses because of the flexibility of mixing different colors, \cite{45} and, in principle, this mechanism also has higher quantum efficiency in producing white light.
1.3 All kinds of EL materials

The advantages of polymeric/organic materials over inorganic materials are high fluorescent efficiency, wide selection of colors and the easiness in the fabrication of large films. Depending on the molecular structure, organic EL materials may be classified into three categories: small molecular EL materials; polymeric EL materials; charge injection/electrode materials.

1.3.1 Small molecular organic EL materials

The typical small molecular EL materials consist of metallic complex and small molecular organic material. The metallic complex, for example, Alq$_3$, BeBq$_2$ and Almq$_3$, has such characteristics as good membrane forming ability, thermal and chemical stability. While the most important property of small molecular organic material is facile molecular design as doping material to emitting film. Usually, to the host material film with good membrane forming ability and poor luminous property, the guest materials
with poor film-forming ability and good luminous property were added or doped, to obtained OLED with balance charge-transport, good film properties and thermal/chemical stability.

Figures 1-6 and 1-7 illustrate the structures of typical metallic complex EL materials and small molecular organic EL materials, while Figures 1-8 and 1-9 show the typical fluorescence and phosphorescence dopant materials, respectively.

**Figure 1-6.** Typical metallic complex EL materials

**Figure 1-7.** Typical small molecular organic EL materials
1.3.2 Polymeric EL materials

The typical polymeric EL materials consist of π-conjugated polymers and unconjugated ones. For π-conjugated polymers, the fluorescent electroluminescence originates from the vibration of π-π conjugated structure of backbone, and the emitting color depends on the band gap energy of polymers. Chromophore groups usually are designed to be blended with or dopped into conjugated/unconjugated polymer backbones as side-chain or end-capper, to obtain EL device with high properties.
1.3.3 Carrier transport material

The carriers (holes and electrons) are injected from electrode, transport through carrier transport material, to emitting layer in the EL process. The carrier transport material should facilitate carrier injection and transport from the electrode, and serve as a layer blocking opposite charge into the electrode. Figures 1-11 and 1-12 show the typical electron- and hole-transporting materials, respectively.
1.3.4 Carrier injection material and electrode material

Recently, fluoride lithium (LiF), alkali metals (Li, Cs), calcium (Ca) and barium (Ba) are used as electron-injection material in EL device via vacuum deposition method. For the hole-injection material, phtharocyanines and arylamines are utilized for OLED and water soluble polymer, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) for PLED.

As for the anode material, indium Tin Oxide (ITO) is commonly used, while magnesium (Mg), silver (Ag) and aluminum (Al) are utilized as cathode materials.
1.4 Polyfluorene

1.4.1 Blue PLED and polyfluorene

Green-, red-, and white-light-emitting materials are generally prepared by introducing appropriate doping components into blue-emitting materials. This approach is based on the wide energy band gap of blue-emitive materials, which means they transfer their energy into red or green dopant materials by Förster and Dexter mechanisms, thereby enabling green, red, and white emission. \[46-47\] Therefore, developing efficient, stable and deep blue PLED is essential to realizing such applications.

A large number of photoactive and electro-conjugated polymer have been introduced for PLED applications in recent decades, such as poly\((p\)-phenylenevinylene) (PPV) \[48-51\], polythiophene (PT) \[52\], and polyfluorene (PF) \[53-56\]. PF and its derivatives are the most promising candidates as blue-light-emitting polymers because they possess a relatively large band gap, have been widely investigated as blue PLED because of
their superior properties, such as highly efficient photoluminescence (PL), excellent thermal and oxidative stability, good solubility in common organic solvents and amenability to functionalization at the 9-position of fluorene. [57-59]

Polyfluorenes are not naturally occurring materials, but could be designed and synthesized with different properties for a wide variety of applications. [60] The luminescent color can be designed through a synthetic control over the electron donating or withdrawing character of the substituents on fluorene or the comonomers in polyfluorenes. [61-63]

1.4.2 The disadvantages and resolves of polyfluorenes

Although possessing excellent properties as suitable PLED materials, polyfluorenes of course have inherent disadvantages.

Polyfluorenes often show both excimer and aggregate formation upon thermal annealing or when current is passed through them [64]. Excimer formation involves the generation of polymer units which emit light at lower energies than the polymer itself. This hinders the use of polyfluorenes for most applications, including light-emitting diodes (LED). When excimer or aggregate formation occurs this lowers the efficiency of the LEDs by decreasing the efficiency of charge carrier recombination. Excimer formation also causes a red shift in the emission spectrum.

Polyfluorenes can also undergo decomposition. There are two known ways in which can occur. The decomposition process involves the oxidation of the polymer
under UV light or electric effect, leads to the formation of an aromatic ketone, quenching the fluorescence.\textsuperscript{[65]}

The incorporation of bulky side functional groups into PFs, shielding the polymer backbone from the formation of aggregates and suppressing interchain interactions, has been reported as an efficient method to resolve this problem.\textsuperscript{[66-69]} In fact, all kinds of modifications were proposed to prepare polyfluorene-based copolymers for the performance improvement, functional groups/structures have been found to play an important role in reducing green emission, among which are anthracene, crosslinkable moieties, hole-trapping groups, sterically hindered groups, polyhedral oligomeric silsesquioxanes, and so on.\textsuperscript{[64]}

Additionally, researchers have tried to add large substituents at the 9-position of the fluorene in order to inhibit excimer and aggregate formation. Aggregation has also been combated by varying the chemical structure. For example, when conjugated polymers aggregate, which is natural in the solid state, their emission can be self-quenched, reducing luminescent quantum yields and reducing luminescent device performance. In opposition to this tendency, researchers have used tri-functional monomers to create highly branched polyfluorenes which do not aggregate due to the bulkiness of the substituent (Figure 1-13). This design strategy has achieved luminescent quantum yields of 42% in the solid state.\textsuperscript{[69]} This solution reduces the ease of processability of the material because branched polymers have increased chain entanglement and poor solubility.
Another serious problem associated with PF is poor electroluminescence (EL) efficiency due to an imbalance in charge carriers due to large hole-injection barriers and different charge carrier mobilities. Electrons transport faster than holes in polyfluorene backbone, the unbalance between the two kinds of charges causes low EL efficiency. Therefore, PF requires additional hole-transporting structure, for example, to obtain balanced and efficient injection and transport for holes and electrons in order to attain high device efficiency in EL device. For example, polytriphenylamine (PTPA), has been found to a) facilitate hole injection and transport from the anode and b) serve as an electron-blocking layer, which blocks electron movement to the anode and confines excitons within the emissive to reduce green emission.\[70-71\]

1.4.3 Polytriphenylamine (PTPA)

Triphenylamines have attracted considerable interest as hole-transport materials in
multilayer organic EL devices for decades because of their relatively high mobilities and their low ionization potentials. The feasibility of using spin-coating and ink-jet printing processes for large-area EL devices and the possibility of various chemical modifications make polymeric materials containing triphenylamine units are very attractive. To enhance the hole injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PFs), there have been several reports on PPV and PF derivatives involving hole transporting units such as triarylamine or carbazole groups in the emissive p-conjugated core/main chains, grafting them as side chains in a polymer and attaching them onto the polymer chain ends or the outer surface of dendritic wedges.

Furthermore, some researchers employed triphenylamine as a polymer backbone for building up the π-conjugated structure of poly(triphenylamine) (PTPA) because PTPA could facilitate hole injection and transport from the anode and block electron movement to the anode. Previously, we reported that PTPA can be synthesized via C-N coupling polymerization of a self-condensing monomer by palladium catalyst. PTPA is allowed via this technique to assemble into the block copolymer architectures by the chain elongation from terminals of the polymer.

For some aromatic emitting polymers, one of the common approaches for increasing the solubility and processability without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups, e.g. triphenylamine, into the backbone. Because of the incorporation of bulky, three-dimensional triphenylamine units along the polymer backbone, all the polymers are amorphous, have good solubility in many aprotic solvents, and exhibited excellent thin-film-forming
1.5 Synthesis method of polyfluorene

The design of polymeric properties requires great control over the structure of the polymer. For instance, low band gap polymers require regularly alternating electron donating and electron accepting monomers. More recently, many popular cross-coupling chemistries have been applied to polyfluorenes and have enabled controlled polymerization; Palladium catalyzed cross couplings such as Suzuki coupling, Heck coupling, etc., as well as nickel catalyzed, Yamamoto, and Grignard coupling reactions have been applied to polymerization of fluorene derivatives.

1.5.1 Nickel(0)-mediated polymerization

One of the methods for preparing poly(arylene)s is dehalogenative coupling reaction of dihaloarenes, which is promoted by nickel(0) complex such as Ni(cod)$_2$ (cod = 1,5- cyclooctadiene). Although this well-established Ni(0)-coupling is undoubtedly the main stream in preparation of π-conjugated poly(arylene)s, there still remain some unavoidable problems: (i) Ni(cod)$_2$ is highly moisture-sensitive, so that the complete removal of moisture from the polymerization system is essential, and (ii) the working-up process is somewhat tedious due to the difficulty in removing the large
amount of nickel residue (generally 1.0 to 1.2 equiv to the monomers).

1.5.2 Suzuki coupling reaction

\[ \text{Suzuki reaction} = \text{cross coupling of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium(0) complex} \]

Figure 1-14. Scheme of Suzuki coupling reaction.

Suzuki reaction is cross coupling of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium(0) complex (Figure 1-14) \[^{116-117}\]. It is widely used for the synthesis of polyfluorene derivatives. Suzuki reaction was awarded to the 2010 Nobel Prize in Chemistry.

Figure 1-15. Mechanism of Suzuki coupling reaction.
The mechanism of the Suzuki reaction is best viewed from the perspective of the palladium catalyst as shown in Figure 1-15. The first step is the oxidative addition of palladium to the halide 2 to form the organopalladium species 3. The reaction with base gives intermediate 4, which via transmetalation with the boronate complex 6 forms the organopalladium species 8. The reductive elimination of the desired product 9 restores the original palladium catalyst 1.

Usually, pyrophoric reagents such as n-butyllithium is used for the conversion of the aryl dihalide to the corresponding borylated or boronic ester monomer, and then the PFs are polymerized with boronic ester or borylating reagent in combination with a palladium catalyst and potassium acetate. However, the borylated or boronic ester comonomers are difficult to purify in many cases, and usually require chromatography to remove unreacted or partially reacted material and byproducts from the reaction \([118-120]\). Recently Miyaura’s group discovered a novel metal mediated reaction by utilizing a hypodiboric ester such as bis(pinacolato)diboron as the borylating reagent in combination with a palladium catalyst and potassium acetate. \([70-71]\) Some reports have utilized other methodologies to form symmetrical and unsymmetrical biaryls via a one-pot Suzuki-Miyaura reaction. Miyaura specifically chose potassium acetate in order to minimize aryl-aryl cross-coupling byproducts and noted that use of other bases such as potassium carbonate lead to significant oligomer formation. \([121]\) All kinds of polymerization conditions, such as structure of the monomer, feed ratio, catalyst, ligand, salt, solvent, temperature, reaction time and additives, were discussed for the polymerization chemistry. \([122-124]\)
1.6 Synthesis of PTPA by Buchwald-Hartwig Cross-Coupling

The direct Pd–catalyzed C-N and C-O bond formation between aryl halides or trifluoromethanesulfonates and amines or between aryl halides or triflates and alcohols (aliphatic alcohols and phenols) in the presence of a stoichiometric amount of base is known as the Buchwald-Hartwig cross-coupling. The coupling can be both inter- and intramolecular. The first palladium catalyzed formation of aryl C-N bonds was reported by T.Migita and co-workers in 1983.[125] More than a decade later in the laboratory of S.Buchwald, a new catalytic procedure was developed based on Migita’s amination procedure.[126]

The great disadvantage of these early methods was that both procedures called for the use of stoichiometric amounts of heat-and moisture-sensitive tributyltin amides as coupling partners. In 1995, S. Buchwald[127] and J. Hartwig[128] concurrently discovered that aminotin species can be replaced with the free amine of used a strong base (eg., sodium tert-butoxide ), which generates the corresponding sodium amide in situ by deprotonating the Pd-coordinated amine. The typical procedure calls for either an aryl bromide or iodide, while the Pd(0)-catalyst is usually complexed with chelating phosphine type ligands such as BINAP, DPPF, XANTPHOS and DPBP or bidentate ligands such as DBA(trans,trans-dibenzylideneacetone). The base has to be present in stoichiometric amounts and the temperature for the reaction can be sometimes as low as 25°C. Since the mid-1990s the reaction conditions for this coupling have gradually
become milder, and by applying the appropriate ligand, even the otherwise unreactive aryl chlorides can be coupled with amines or alcohols.

![Scheme of Buchwald-Hartwig reaction](image)

**Figure 1-16.** Scheme of Buchwald-Hartwig reaction.

![Mechanism of Buchwald-Hartwig reaction](image)

**Figure 1-17.** Mechanism of Buchwald-Hartwig reaction.
1.7 Atom Transfer Radical Polymerization (ATRP)

A new concept of living polymerization based on the reversible stabilization of growing radical by covalent species was reported. [129-132] Although the system needs further optimization, it is worth giving here some of the preliminary findings. So-called atom transfer radical polymerization (ATRP) is analogous to atom transfer addition reaction used in organic synthesis [133] and involves the reversible hemolytic cleavage of a carbon-halogen bond by redox reaction between an organic halide(R-X) and transition metal, e.g., copper (I) salts, as illustrated in Eq.(1).

The "living nature of the process arises from two phenomena: (a) the low stationary concentration of growing radicals and (b) the reversible equilibrium of propagation and deactivation. If the deactivation process does not occur or is very slow, the polymerization becomes a conventional redox initiated polymerization; transfer an termination reaction may be operative. When one monomer unit is added at each activation in an insertion manner, the process is well controlled. Depending on catalysts, both heterogeneous and homogeneous polymerizations may be performed with slight differences in polydispersities. [134]

Kinetic studies [135] performed with homogeneous catalysts revealed that the rate of polymerization is first order with respect to monomer and alkyl halide initiator and is usually negative first order with respect to the deactivator and transition metal.
complexed by two bipyridine ligands. Kinetics depend on the radical propagation rate constant $k_p$ and equilibrium constant $K_{eq} = K_{act} / K_{deact}$.

\[
\begin{align*}
    \text{Mt}^m/L_n + R-X & \xrightarrow{k_{act}} X-\text{Mt}^{m+1}/L_n + R \quad +M \\
    \text{Mt}^m & \text{transition metal} \\
    L_n & \text{complexing ligand} \\
    R & \text{polymer chain} \\
    X & \text{Br or Cl}
\end{align*}
\]

**Figure 1-18.** Mechanism of atom transfer radical polymerization (ATRP)

1.8 **Aim of this thesis**

In order to achieve the large area of EL display and lighting in commercial applications, it is essential to fabricate the devices in a low cost. Therefore wet-processes such as spin-coating and ink-jet with polymeric materials are promising. As discussed above, polymeric devices generally show lower performance (efficiency, life time) compared with devices fabricated with a vacuum process based on low-molecular weight materials.

Low efficiency in polymeric devices is partially due to difficulty in fabricating the devices with a layered-structure. To overcome the drawbacks, a breakthrough is
necessary from the point of the molecular design and the control the morphology in the active layer. The author’s research group has showed the advantage of block copolymers consisting of hole and electron transporting blocks as the host materials in phosphorescent devices. Block copolymers were prepared via a nitroxide mediated living radical polymerization (Figure 1-19).

More recently Tan et al. synthesized the different type of block copolymers for EL applications via the Suzuki coupling polymerization followed by the C-N coupling polymerization, which consisted of light emitting and electron transporting polyfluorene (PF) unit and hole transporting polytriphenylamine (PTPA) unit. It was revealed that the introduction of PTPA increased emission efficiencies compared with PF homopolymer. This is due to the facile hole injection from the anode and/or the efficient electron block by PTPA moieties, which are located in the vicinity of the PEDOT/PSS coated on the
anode through the hydrogen bonding of trioxyethylene group with PSS (Figure 1-20).

Figure 1-20. Structure of PTPA-b-PF-b-PTPA triblock copolymer

The aim of this thesis is to propose the novel methodology for the increase of the efficiency in POLED. The molecular design of block copolymers and the morphology control are not enough for the practical applications. The author tried two approaches. The first one is the novel molecular design of full functional polymers, which are block copolymers consisting of hole transporting unit and electron transporting unit with emitting moiety at the junction point. Second one is the morphology control of blend systems consisting of homopolymer(s) and corresponding block copolymer in order to optimize the morphology in EL active thin films.

In the previous devices utilizing block copolymers as host polymers, emitting materials are low-molecular weight phosphorescent dyes dispersed in host materials. In this case, emitting parts are randomly distributed in the active layer. Emission process is resulted from the recombination of holes and electrons, followed by the energy transfer from recombination centers to emitting moieties. Therefore if the emitting parts are located in the vicinity of the interface between hole and electron transporting domains, more efficient energy transfer is anticipated. In order to attain the situation, a new
molecular design is proposed. The detail of molecular design in the first approach is as follows.

Target polymers are block copolymers consisting of hole transporting unit and electron transporting unit with emitting moiety at the junction point as shown in Figure 1-21. If an ideal phase separation occurs, the emitting moiety exists at the interface between both domains.

![Figure 1-21. Concept of this thesis](image)

When the block copolymer is composed with the same type of monomers (e.g. vinyl monomers), it is generally difficult to introduce the functionality at the junction. Synthetic strategy is the utilization of bi-functional initiators possessing an emitting moiety. Bi-functional initiators provide two types of initiating sites via different polymerization mechanism as shown in Figure 1-22.
Typical phase separated morphologies in the block copolymer (similar A/B volume ratio) thin films (80-100 nm thick) are shown in Figure 1-23, which are bi-layered (a), multi-layered (b), vertically oriented lamella (c), and bulk hetero junction type structures. For EL applications, bi-layer structure seems ideal. For the effective hole and electron injection, the hole transporting layer should be on the side of anode (generally ITO covered glass coated with PEDOT/PSS), and the electron transporting layer should be on the cathode side (aluminum is deposited on the top of the film).

**Figure 1-22.** Concept of bi-functional initiator to introduce the functionality at the junction point.

**Figure 1-23.** Various possible morphologies in block copolymer thin films
To attain this structure, two important points should be considered. As mentioned above Tan proposed the strategy that the hole transporting moiety is chemically modified to afford the attractive interaction with hydrophilic PEDOT/PSS. This type of chemical modification for one block is the primary important point for bi-layered structure. The second important point is the control of the domain size. Generally the domain size is dependent on the molecular mass for each block. However, it is not feasible to obtain such a high molecular mass polymers corresponding to 40 – 50 nm of thickness. Therefore in this thesis, the blend system consisting of homopolymer(s) and block copolymer is investigated to elucidate the relationship between the domain size and EL performance. The domain size of phase separation in blend systems can be decreased by the addition of block copolymer.

1.9 Outline of this thesis

The author’s goal is to develop conjugated polyoxadiazole-phenothazine- block-polytriphenylamine (PBD-Ph-\textit{b}-PTPA) diblock copolymers, and polytriphenylamine-phenoxazine-block-polyfluorene-block-phenoxazine-polytriphenylamine (PTPA-Ph-\textit{b}-PF-\textit{b}-Ph-PTPA) triblock copolymers and to evaluate EL devices based on the designed polymers. EL devices based on the blend consisting of PTPA–\textit{b}-PF, PF, and PTPA were also fabricated.

In Chapter \textbf{2}, 2-(4-\textit{t}-butylphenyl)-5-(4-vinyl biphenyl-4’-yl)-1,3,4-oxadiazole (PBD monomer) and 4-(4’-Bromobiphenyl)-4-n-butyldiphenylamine (TPA monomer) were synthesized. At first the author synthesized bifunctional initiator with an emitting
moiety, phenylphenothiazine. In polymerization of TPA block Buchwald-Hartwig C-N coupling reaction via Pd(0) was adopted while atom transfer radical polymerization was adopted polymerization of PBD block. PTPA homopolymers and PTPA-phenothiazine-b-PBD copolymers were characterized with GPC and $^1$H NMR, which confirm the structure of obtained product. The photophysical properties were examined by UV absorption and PL emission analysis both in solution and in thin film. The electrochemical properties were also examined at the end.

In Chapter 3, 2,7-dibromo-9-(4-methylphenyl)-9-(4-octylphenyl)fluorene (fluorene monomer) and 4-(4’-Bromobiphenyl)-4-n-butyldiphenylamine (TPA monomer) were synthesized. PF block was synthesized via Suzuki-Miyaura coupling polymerization and capped with phenoxazine emitting group, and PTPA block was synthesized via Buchwald-hartwig C-N reaction, and finally PTPA-phenoxazine-b-PF-b-phenoxazine-PTPA was synthesized successfully.

PF homopolymers and PF-b-PTPA copolymers were characterized with GPC and $^1$H NMR, which confirm the structure of obtained product. The photophysical properties were examined by UV absorption and PL emission analysis both in solution and in thin film. The electrochemical properties were also examined at the end.

In Chapter 4, electroluminescent devices based on the blend consisting of PF, PTPA homopolymers and PF-PTPA block copolymers (without phenoxazine emitting part) were fabricated and the current density - voltage - luminance (L) characteristics were evaluated for the devices. EL performance was discussed with the film morphologies observed by AFM.

Finally, in Chapter 5, general conclusions about the study are described.
1.10 References


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Chapter 2. Synthesis of polytriphenylamine and polyoxadiazole block copolymer with emitting part at junction for light emitting application

2.1 Introduction

Polymeric organic light-emitting diode (POLED) device has a number of advantages over conventional displays such as high brightness, high contrast, low-voltage operation, large viewing angle, and extremely thin device. Numerous efforts on investigation for light emitting materials have been done for decades, thus the market for organic light emitting diode (OLED) applications has been getting larger and larger.\(^1\)

Polymeric light emitting materials have been attracted much attention because of good suitability for easy processing such as spin coating and ink-jetting techniques. Now days, phosphorescent system dispersing a dopant such as Ir complex or highly emitting low molecules in polymer matrix prevails over other polymeric devices in external quantum efficiency (EQE)\(^2-6\), but still remains behinds compared with multi-layer organic small molecular devices fabricated by chemical vapor deposition. Single-layer polymer OLED device created by a wet process can be an excellent candidate for mass production of devices, if EQE is improved.
Copolymer or polymer blend systems consisting of several functional units such as hole and electron transporting components have been studied by many researchers.\textsuperscript{[7-10]} In polymer blend systems one or more polymers are blended with other optional dopants and solution-deposited onto device substrates. Whilst this approach has the benefit of simplifying the synthesis to arrive at multiple components, problems can arise if crystallization and film morphology changes occur during device operation. An example is provided by combination of the fluorescent heptacene derivative doped into a polyfluorene host, in a spin coated, two-compartment, single-emissive layer structure.\textsuperscript{[11]} In recent works, it was demonstrated that the device performance based on bipolar charge transporting block copolymers was significantly influenced by phase-separated morphology in the polymer layer, and that the nanophase separation of block copolymers facilitated charges recombination due to lowering charge transport in the emitting layer, resulting in high EQE compared to the random copolymer systems without such a structure.\textsuperscript{[12-14]}

In our previous work works in the author’s research group, block copolymers comprising triphenylamine and fluorinated oxadiazole units as hole and electron transport segments, respectively, were prepared to construct pseudo-layered structure by assembling oxadiazole segment in the vicinity the air surface. In these devices, emitting materials are low-molecular weight phosphorescent dyes dispersed in host materials. In this case, emitting parts are randomly distributed in the active layer.\textsuperscript{[15-16]}

In this chapter the author synthesized the block copolymer consisting of hole
transporting polytriarylamine and electron transporting polyoxadiazole with the light emitting phenothiazine unit\textsuperscript{[17]} at the junction of both segments. As described in Chapter 1, when the block copolymer is composed with the same type of monomers (e.g. vinyl monomers), it is generally difficult to introduce the functionality at the junction. Synthetic strategy is the utilization of bi-functional initiators possessing an emitting moiety. Bi-functional initiators provide two types of initiating sites via different polymerization mechanism. It is expected that prepared block copolymers are promising candidates for efficient EL devices, where emitting sites are well controlled utilizing the self-assembly ability. If the emitting parts are located in the vicinity of the interface between hole and electron transporting domains, more efficient energy transfer is anticipated. In order to attain the situation, a new molecular design is proposed.

2.2 Experimental

2.2.1 Materials

All reagents and solvents were used without further purification unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium and benzophenone, and stored under nitrogen atmosphere. Toluene was distilled over calcium hydride, and
stored under nitrogen atmosphere. Chloroform-D and DMSO-d$_6$ were used as solvents for $^1$H NMR, and chloroform was used as an eluent for gel permeation chromatography (GPC) measurements.

2.2.2 Synthesis

2.2.2.1 4-bromobenzoic hydrazide(1)

To a three-necked flask equipped with a stopcock and a condenser were added ethyl 4-bromobenzoate (25.0 g, 109 mmol), hydrazine monohydrate (40.0 mL, 825 mmol), and methanol (220 mL) under nitrogen atmosphere, and the mixture was stirred at 40°C for 16 h. After the concentration, the precipitation was collected by vacuum filtration and washed with water. The yield was 20.3 g (86.6%). $^1$H NMR (DMSO-d$_6$):

δ 9.79 (s, 1H), 7.75 (d, 2H), 7.65 (d,2H), 4.47 (s, 2H).

2.2.2.2 1-(4-t-butylnzoyl)-2-(4-bromobenzoyl)hydrazine(2)

To a two-necked flask equipped with a stopcock and an additional funnel were
added 1 (20.0 g, 93.0 mmol) and pyridine (250 mL) under nitrogen atmosphere. The solution of \( t \)-butylbenzoyl chloride (18.3 g, 93.0 mmol) in pyridine (100 mL) was added dropwise at 0°C, and then the mixture was stirred for 3 h. After an additional stirring was continued for 3 h at room temperature, excess amount of water was added to precipitate the product. The white solid was filtered and washed with water. The yield was 22.1 g (94.8%). \(^1\)H NMR (DMSO-\( d_6 \)): \( \delta \) 10.41 (s, 2H), 7.86 (d, 4H), 7.72 (d, 2H), 7.52 (d, 2H), 1.31 (s, 9H).

2.2.2.3 2-(4-bromophenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole(3)

To a two-necked flask equipped with a stopcock and a condenser were added 2 (33.0 g, 87.9 mmol) and phosphorous oxyhydrochloride (200 mL) under nitrogen atmosphere, and the resulting mixture was stirred at 100°C for 20 h. After cooling down to room temperature, excess phosphorous oxychloride was removed under vacuum. Water was added to the residue, and the precipitate was filtered and washed with water. The white crystal was obtained by recrystallization from ethanol. The yield was 20.0 g (63.7%). \(^1\)H NMR (DMSO-\( d_6 \)): \( \delta \) 8.02(d, 4H), 7.80(d, 2H), 7.62 (d, 2H), 1.33 (s, 9H).
2.2.2.4 2-(4-t-butylyphenyl)-5-(4-vinylphenyl-4’-yl)-1,3,4-oxadiazole (4)

To a two-necked flask equipped with a condenser were added 3 (4.65 g, 13.0 mmol), 4-vinylphenylbronic acid (2.00 g, 13.5 mmol), tetrakis(triphenylphosphine)palladium(0) (0.312 g, 0.27 mmol), and dry THF (15.0 mL) under nitrogen. After the solution of potassium carbonate (3.74 g, 27.1 mmol) in oxygen-free water (13.5 mL) was added, the mixture was stirred at 70 °C for 24 h. The resulting mixture was extracted with chloroform, and the organic layer was dried with magnesium sulfate and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography eluted with chloroform/ethyl acetate (95/5) followed by recrystallization from methanol to yield the white crystal. The yield was 2.99 g (60.5%).

\[\text{H NMR(CDC}_3\text{)}: \delta\ 8.21 (d, 2H), 8.09 (d, 2H), 7.77 (d, 2H), 7.64 (d, 2H), 7.57 (d, 2H), 6.78(dd, 1H), 5.84 (d, 1H), 5.32 (d, 1H), 1.38 (s, 9H).

2.2.2.5 4-(4’-bromobiphenyl)-4”-n-butyldiphenylamine (5)

To a 30-mL flask equipped with a stopcock and a condenser were placed
4-butylationine (2.89 mL, 20 mmol), 4,4’-dibromobiphenyl (6.24 g, 20 mmol), sodium tert-butoxide (2.69 g, 28 mmol), Pd(dppf)Cl$_2$ (0.163 g, 0.2 mmol), and toluene (5 mL) under nitrogen atmosphere. After reaction for 24 h under reflux, the mixture was washed with 1 N HCl and brine. The organic layer was dried with MgSO$_4$ and concentrated by rotary evaporator. The crude product was purified by column chromatography (hexane : ethyl acetate = 1:5). Reddish brown solid was obtained. The yield was 4.74 g (62.4%).

Mp: 116°C (DSC).$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.51 (d, 2H), 7.43 (d, 2H), 7.41 (d, 2H), 7.11 (d, 2H), 7.07 (d, 2H), 7.04 (d, 2H), 5.71 (s, 1H), 2.57 (t, 2H), 1.59 (m, 2H), 1.37 (m, 2H), 0.93 (t, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 143.91, 140.02, 139.90, 136.80, 131.94, 131.75, 129.40, 128.18, 127.93, 120.65, 119.38, 116.94, 35.06, 33.92, 22.44, 14.09. Anal. Calcd for C$_{22}$H$_{22}$BrN: C, 69.48; H, 5.83; N, 3.68. Found: C, 69.54; H, 5.87; N, 3.71.
Scheme 2-1. Synthesis route of 4-(4-"t"-butylphenyl)-5-(4-vinylphenyl-4′-yl)-1,3,4-oxadiazole

Scheme 2-2. Synthesis route of 4-(4′-Bromobiphenyl)-4-n-butylidiphenylamine
Scheme 2-3. Synthesis route of two functional initiator with emitting part and protected by silyl group
Scheme 2-4. Synthesis route of 4-(4′-bromophenyl)- 4”-n-butyldiphenylamine and PTPA- phenyl- phenothiazine$^{[18]}$
2.2.2.6 4-bromo-o-cresol (6)

To a two-necked flask were added 2-methylphenol (1.8 g, 16.6 mmol), tetrabutylammonium tribromide (7.9 g, 16.87 mmol), dichloromethane (60 mL), and methanol (40 mL). The reaction mixture was stirred for 30 min in 0 °C, and then stirring was continued for 6 h at room temperature. After removing the solvents, the product was dissolved in dichloromethane and washed with water for more than 10 times and dried under MgSO₄ and concentrated by a rotary evaporator to yield white crystal. The yield was 2.40 g (77.00%). ¹H NMR (300 MHz, CDCl₃): δ 1.97 (m, 1H), 2.21 (s, 3H), 6.66 (d, 1H), 7.18 (d, 1H), 7.2 (s, 1H)

2.2.2.7 2-(4-bromo-2-methylphenoxy)ethanol (7)

To a two-necked flask equipped with a stopcock and a condenser were added 6 (5.10 g, 27.00 mmol), 2-chloroethanol (22 g, 273 mmol), NaOH (10%) solution (120 mL), and the mixture was stirred for 24 h under N₂ atmosphere. Then dichloromethane was added to the mixture, and the mixture was washed with NaOH solution (10%) twice and water three times, successively. The organic layer was washed by MgSO₄ and concentrated by a rotary evaporator and recrystallized in hexane to yield white crystal. The yield was 5.10 g (80.9%). ¹H NMR (300 MHz, CDCl₃): δ 1.97 (m, 1H), 2.21 (s, 3H), 3.95 (t, 2H), 4.07 (t, 2H), 6.66 (d, 1H), 7.18 (d, 1H), 7.2 (s, 1H)
2.2.2.8 2-(4-Bromo-2-bromomethyl-phenoxy)-ethanol  (8)

To a two-necked flask equipped with a stopcock and a condenser were added 7 (1.827 g, 7.90 mmol), NBS (1.345 g, 7.9 mmol), AIBN (0.022 g, 0.13 mmol) and carbon tetrachloride (87 mL) and the mixture was refluxed at 70 °C for 24 h. After the evaporation of the solvent, the product was dissolved in dichloromethane, and the solution was washed with water for more than three times. The organic layer was dried with magnesium sulfate and concentrated by a rotary evaporator to yield white crystal. The yield was 1.167 g (46.8%). ¹H NMR (300 MHz, CDCl₃): δ 1.97 (m, 1H), 4.49 (s, 2H), 3.95 (t, 2H), 4.07 (t, 2H), 6.66 (d, 1H), 7.18 (d, 1H), 7.2 (s, 1H)

2.2.2.9 [2-(4-Bromo-2-bromomethyl-phenoxy)-ethoxy]-tert-butyl-dimethyl-silane (9)

To a two-necked flask equipped with a stopcock and a condenser were added 8 (3.10 g, 13.4 mmol), tert-butyldimethyl chlorosilane (1.956 g, 13.40 mmol), DMAP (0.01 g, 0.08 mmol), dichloromethane (50 mL), and the mixture was stirred for 30 min at 0 °C. Then, pyridine (1.1 mL) was added dropwise to the mixture very slowly, and after 30 min the temperature was elevated to room temperature, and stirring was continued for 24 h. After the reaction, the solvents were removed, and the product was dissolved in DEE. The solution was washed with water for 3 times and dried with
magnesium sulfate and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography eluted with chloroform to yield product. The yield was 3.67 g (72.4%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.08 (s, 6H), 0.81(s, 9H), 4.49(s, 2H), 3.95 (t, 2H), 4.07 (t, 2H), 6.66 (d, 1H), 7.18(d, 1H), 7.2(s, 1H)

2.2.2.10 Phenylphenothiazine with methoxy group (10)

To a 30-mL flask equipped with a stopcock and a condenser were placed phenothiazine (1.0 g, 5.01 mmol), 4-bromoanisole (0.93 g, 5.01 mmol), sodium tert-butoxide (0.57 g, 6.01 mmol), Pd(OAc)$_2$ (0.02 g, 2 mol%), P(t-Bu)$_3$ (0.08 g, 8 mol%) and toluene (5 mL) under nitrogen atmosphere. After the reaction under reflux for 24 h, the mixture was washed with water three times, and the organic layer was dried with magnesium sulfate and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography with toluene/hexane (6:1) to yield product. The yield was 1.31 g (85.0%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 3.90 (s, 1H), 6.19 (d, 2H), 6.81 (m, 4H), 6.99 (d, 2H), 7.12 (d, 2H), 7.31 (d, 2H).

2.2.2.11 phenylphenothiazine with hydroxyl group (11)

To a 10-mL flask equipped with a stopcock were placed 10 (0.15 g, 0.50 mmol) and CH$_2$Cl$_2$ (4 mL), and the mixture was cooling down to -78 °C, and then BBr$_3$ (4 mL of 1M CH$_2$Cl$_2$ solution) was added dropwise very slowly. After 2 h, the mixture was
warmed up to room temperature, and stirring was continued for 24 h. After the reaction, 
the excess BBr3 was quenched with water, and the product was dilute with 
dichloromethane. The solution was washed with water three times and dried with 
magnesium sulfate, and concentrated by a rotary evaporator. Drying under vacuum 
afforded the product. The yield was 0.13 g (89.2%). ¹H NMR (300 MHz, CDCl₃): δ 
5.30 (s, 1H), 6.19 (d, 2H), 6.81 (m, 4H), 6.99 (d, 2H), 7.12 (d, 2H), 7.31 (d, 2H).

2.2.2.12 Initiator with emitting unit and protective group  (12)

To a 10-mL flask equipped with a stopcock and a condenser were placed 11 (0.5 g, 
1.69 mmol), 9 (0.64 g, 1.53 mmol), potassium carbonate (0.92 g, 6.6 mmol) and acetone 
(5 mL). The mixture was refluxed under nitrogen atmosphere for 48 h. After the 
reaction, the solvent was removed, and the product was dissolved in chloroform. The 
solution was washed with water three times, and the organic layer was dried with 
magnesium sulfate and concentrated by a rotary evaporator. The crude product was 
purified by silica gel column chromatography with chloroform to yield the product. The 
yield was 0.713 g (82.2%). ¹H NMR (300 MHz, CDCl₃): δ 0.08 (s, 6H), 0.80(s, 9H), 
3.91 (t, 2H), 4.02 (t, 2H), 6.12 (d, 2H), 6.71 (d, 1H), 6.74 (m, 4H), 6.9 (d, 2H), 7.12 (d, 
2H), 7.24 (d, 2H), 7.32 (d, 1H), 7.57 (d, 1H).
2.2.2.13 Polytriphenylaminine end functionalized with phenylphenothiazine (13)

In a 10-mL two-necked round-bottom flask under nitrogen atmosphere, initiator 12 (0.14 g, 0.22 mmol) which was prepared as described in Scheme 2-3, Pd(OAc)$_2$ (0.0098 g, 2 mol%), P($t$-Bu)$_3$ (0.356 g, 8 mol%) and THF (2 mL) were added, and the mixture was stirred to obtain a clear solution. In the other 10-mL two-necked round-bottom flask under nitrogen atmosphere, monomer 5 (0.84 g, 2.2 mmol), sodium $t$-butoxide (0.25 g, 2.6 mmol) were dissolved in 2 mL of THF, and to this solution was added the previous prepared solution of the initiator. After stirring under reflux for 24 h, diphenylamine (100 mg, 0.59 mmol) in 1 mL of THF was added, and further reflux was continued for 6 h. After cooling, the reaction mixture was poured into to excess amount of methanol for precipitation, and the precipitate was collected. The product was washed with acetone and water followed by drying under vacuum. The yield was 0.71 g, (86.9%).

2.2.2.14 deprotecting reaction of 13 (14)

In a round bottom flask were placed 13 (0.06 g, 0.0048 mmol), THF (6 mL). To this solution, HF(pyridine solution, 8 drop) was added dropwise at 0 °C. After 30 min the mixture was warmed up to room temperature, and stirring was continued for 24 h.
After the reaction, the mixture was poured into excess amount of methanol for precipitation, and the precipitate was collected and was washed with acetone. The yield was 0.058 g (100%).

2.2.2.15 Macro initiator for ATRP reaction (15)

In a 10-mL round bottom flask equipped with a stopcock flask were placed 14 (0.058 g, 0.0048 mmol), THF (5 mL), TEA (0.5 mL, 3.7 mmol), and the mixture was stirred for 30 min to dissolve the polymer completely under nitrogen atmosphere. The solution was cooled down to 0 °C and stirred for 30 min and 2-bromopropionyl bromide (0.3 mL, 3.4 mmol) was drop wise very slowly. After 30 min the mixture was warmed up to the room temperature and stirred for 48 h. After the reaction the mixture was poured into excess amount of methanol for precipitation, and the precipitate was collected and was washed by acetone. The yield was 0.059 g (100%).

2.2.2.16 Block copolymer with emitting part at junction (16)

To a two-necked 10-mL flask equipped with a stopcock and a condenser were placed 15 (0.036 g, 0.01 mmol), oxadiazole monomer, 4 (0.028 g, 0.08 mmol), CuBr (0.007 g, 0.05 mmol), 2,2’-bipyridyl (0.012 g, 0.07 mmol), o-dichlorobenzene (2 mL). After the dissolution of all contents, the flask was sealed under vacuum, and then the “freeze-pump-thaw” cycle was carried out three times to remove oxygen from the flask.
containing reactants. The mixture was refluxed for 72 h at 140 °C under nitrogen atmosphere. After the reaction, the mixture was poured into excess amount of methanol for precipitation, and the precipitate was collected. The yield was 0.011 g.

Scheme 2-5. Synthesis route of Block copolymer with emitting part at junction
2.3 Results and discussion

2.3.1 Syntheses of monomeric compounds

Oxadiazole monomer, 4 to build the electron transporting block was synthesized via four step reactions as shown in Scheme 2-1.\textsuperscript{[16]} Figure 2-1 shows $^1$H-NMR spectrum of brominated oxadiazole derivative (3) synthesized by the cyclodehydration of 1,2-diacetylhydrazine, 2 using phosphorous oxychloride (POCl$_3$) as a dehydrating agent. Subsequent Suzuki coupling reaction afforded the vinyl monomer, 4 as shown in Figure 2-2. Monomer 5 for hole transporting block, was synthesized by Buchwald-Hartwig coupling reaction.\textsuperscript{[18, 19]} Formation of 5 was confirmed by $^1$H, and $^{13}$C NMR as shown in Figure 2-3.
Figure 2-1. $^{1}$H-NMR of 2-(4-bromophenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole
Figure 2-2. $^1$H-NMR of 2-(4-t-butylphenyl)-5-(4-vinylphenyl-4'-yl)-1,3,4-oxadiazole
The key material in this chapter is the bifunctional initiator with an emitting moiety, compound 12. This compound can initiate both C-N coupling, and atom transfer
radical polymerizations (after post-modification) with fluorescent phenylphenothiazine moiety. The synthetic route of this initiator was shown in Scheme 2-3. In order to obtain precursor 9, o-cresol was mono-brominated utilizing the mild reagent for bromination to avoid dibromination. After Williamson reaction with 2-chloroethanol, radical type bromination reaction at methyl group was conducted with NBS/AIBN followed by the protection of hydroxyl group with t-butyldimethylsilyl group leading to 9. N-(4-Methoxyphenyl)phenothiazine (10) (Figure 2-4 was synthesized Buchwald-Hartwig coupling reaction of phenothiazine with 4-bromoanisole, and the cleavage of ether linkage was conducted by BBr₃ to afford 11. Finally the coupling reaction of 9 with 11 gave the bifunctional initiator (12) (Figure 2-5)

![Figure 2-4. ^1H NMR of phenylphenothiazine with methoxy group](image-url)
2.3.2 Syntheses of polymers

Our group has reported a self-condensing type monomer 5 with bromophenyl and diphenylamine moieties for building up well-defined polymer via C-N coupling reaction, which could be functionalized at both terminals separately by adding terminal modifying derivatives like an aryl bromide or arylamine derivatives as a terminator.\(^{[19]}\) As a result, PTPA-b-poly(ethylene oxide)\(^{[19]}\) and PTPA-b-polystyrene\(^{[20]}\) were
synthesized using polymer modified aryl bromides as terminal modifiers. However a previous study revealed that the preparation of PTPA-\(b\)-poly(\(n\)-butylacrylate) (PBA) via C-N coupling polymerization in the presence of a terminal modifier with PBA chain or ATRP initiating 2-bromopropionate moiety afforded PTPA homopolymer without designed chain end in a relatively low yield.\(^{[21]}\) This is probably due to the prohibition of oxidative insertion of Pd by the ester groups. For the preparation of PTPA-\(b\)-PBA, different synthetic strategy was adopted.\(^{[21]}\) Aryl bromide with hydroxyl group protected with \(t\)-butyldimethylsilyl group was used as an initiator (terminal modifier) to afford end-functionalized PTPA followed by the deprotection and the esterification with 2-bromopropionoyl bromide. With resulting macroinitiator, ATRP of BA was carried out in order to obtain the target block copolymer. In this chapter, the author also adopted the similar synthetic strategy.

In the first step, C-N coupling polymerization of 5 was conducted with the initiator 12. The polymerization was carried out using palladium acetate and \(\text{tr}i(\text{\textit{tert}}\text{-butyl})\text{phosphine ligand as the catalyst, and \textit{tert}-butoxide as base in THF for 24 h.}\) Figure 2-6a shows \(^1\text{H-NMR spectrum of precursor 13.}\) All the signals can be assigned, including the PTPA chain and TBS end group. Moreover, no signal derived from the diphenylamino terminal at 5.7 ppm can be found, which indicated the complete modification of diphenylamino group by 12. Deprotection of TBS group of 13 was conducted using pyridine/HF in the THF solution. After the reaction, precipitations from methanol
and acetone were carried out to get rid of the low molecular weight by-products. The conversion of the TBS group to hydroxyl group was confirmed by the complete disappearance of signals for methyl protons at 0.11 ppm and 0.9 ppm in $^1$H-NMR (Figure 2-6b). The PTPA with hydroxyl end group (14) was esterified with 2-bromopropionyl bromide. The structure of the PTPA with bromo ester end group (15) which used as a macroinitiator of ATPR was confirmed by $^1$H NMR. As shown in Figure 2-7, all signals were reasonably assigned.

Finally, preparation of diblock copolymers containing oxadiazole moiety was carried out by ATRP using CuBr as a catalyst, bipyridyl as a ligand and bromoester terminated PTPA as a macroinitiator. It is known that the typical ATRP is conducted in bulk. However, since monomer 4 is solid, o-dichlorobenzene was used as the solvent. As shown in Figure 2-8, signals from oxadiazole moiety appeared 8.0-8.2 ppm indicating the introduction of oxadiazole units in the polymer. The mole ratio of PTPA/PBD was estimated to be 6/5. Figure 2-9 shows the GPC chromatograms of the macroinitiator and the block copolymer. GPC system was calibrated with polystyrene standards. Although both polymers contain some low molecular weight impurity, it is found that ATRP brought about the increase of molecular weight. The number average molecular weights for the homopolymer and the block copolymer are 500 and 1900, respectively.
Figure 2-6. $^1$H NMR of polytriphenylaminine end functionalized with phenylphenothiazine with (a) and without (b) silyl protective group.
Figure 2-7. $^1$H NMR of macroinitiator for ATRP
Figure 2-8. $^1$H NMR of block copolymer with emitting part at junction (16)
2.3.3 Optical properties of synthesized polymers

Figure 2-10 shows optical properties of synthesized polymers. As shown in Figure 2-10a, the block copolymer shows absorption maxima at 314 and 375 nm. Absorption spectrum is almost the same as that obtained by superimposing spectra of both segments.\textsuperscript{[16,19]} Both polymers exhibited almost the same PL spectra as shown in Figure 2-10b. The contribution of phenothiazine unit was almost negligible.
a) UV

![UV spectrum of polymers](image)

b) PL

![PL spectrum of polymers](image)

**Figure 2-10.** Optical properties of PTPA-block-PBD with emitting part at the junction

Chloroform solution (0.01 mg/mL). Excitation (in PL measurements): 314 nm
2.4 Conclusions

A novel synthetic method was proposed for the bifunctional block copolymer where the junction point possesses different function. The block copolymer consisting of hole transporting polytriaarylamine (PTPA) and electron transporting polyoxadiazole with the light emitting phenothiazine unit at the junction of both segments was successfully prepared. PTPA homopolymer with phenothiazine emitting part at the terminal was synthesized via Buchwald-Hartwig coupling reaction using newly designed bifunctional initiator. Resulting PTPA was converted to the macroinitiator for ATRP. Vinyl monomer possessing oxadiazole unit was polymerized to afford the expected block copolymer with phenothiazine emitting part at the junction. Synthesized polymers were readily soluble in common organic solvents, and readily formed thin film by a solution processing. All of the polymers exhibited an absorption around 315-371 nm both in chloroform solutions, and the PL emission were observed at 421-426 nm in the range of blue-light wavelength.
2.5 References


Chapter 3. Synthesis of Polyfluorene-Polytriarylamine Block Copolymer with Emitting Part at Junction Point for Light Emitting applications

3.1 Introduction

Polymer light-emitting diodes (PLEDs) have attracted much scientific and technological research interest since their first discovery in 1990 \cite{1}. Utilization of electroluminescent polymeric materials shows several advantages over organic small molecules for use in LEDs: better processability, and high flexibility \cite{2}. Furthermore, inexpensive wet-processes such as spin-coating and ink-jet can be applied for the fabrication of PLED devices, which is essential in order to apply PLEDs to display and lighting technologies.

Unfortunately it is generally recognized that polymeric devices generally show lower performance (efficiency, life time) compared with devices fabricated with a vacuum process based on low-molecular weight materials. Low efficiency in polymeric devices is partially due to difficulty in fabricating the devices with a layered-structure. To overcome the drawbacks, a breakthrough is necessary from the point of the molecular design and the control the morphology in the active layer. We have showed the advantage of block copolymers consisting of hole and electron transporting blocks
as the host materials in phosphorescent devices \(^{[3-5]}\). Block copolymers were prepared via a nitroxide mediated living radical polymerization.

Block copolymers assemble into micro- or nano-phase separated structures with various domain shapes such as lamella, cylinder, or sphere. Exploiting nanostructures of block copolymers with appropriate designs can improve performance of applications due to allocation of functionality to each domain \(^{[6]}\). The other groups also reported several block copolymers for PLED applications \(^{[7, 8]}\).

More recently Tan et al. synthesized the different type of block copolymers for EL applications via the Suzuki coupling polymerization followed by the C-N coupling polymerization \(^{[9, 10]}\), which consisted of light emitting and electron transporting polyfluorene (PF) unit and hole transporting polytriarylamine (PTAA) unit. It was revealed that the introduction of PTAA increased emission efficiencies compared with PF homopolymer. This is due to the facile hole injection from the anode and/or the efficient electron block by PTAA moieties, which are located in the vicinity of the PEDOT/PSS coated on the anode through the hydrogen bonding of trioxyethylene group with PSS \(^{[10]}\).

Here we propose the novel methodology for the increase the efficiency in PLED. That is the novel molecular design of full functional polymers, which are block copolymers consisting of hole transporting unit and electron transporting unit with emitting moiety at the junction point. In the previous devices utilizing block copolymers as host polymers, emitting materials are low molecular weight phosphorescent dyes.
dispersed in host materials. In this case, emitting parts are randomly distributed in the active layer. Emission process is resulted from the recombination of holes and electrons, followed by the energy transfer from recombination centers to emitting moieties and/or the charge trap predominately occurred at the emitting sites. Therefore if the emitting parts are located in the vicinity of the interface between hole and electron transporting domains, more efficient energy transfer and carrier trap are anticipated. In order to attain the situation, a new molecular design is proposed. Target polymers are block copolymers consisting of hole transporting unit and electron transporting unit with emitting moiety at the junction point. If an ideal phase separation occurs, the emitting moiety exists at the interface between both domains.

In this study, the synthetic strategy we established for PF-b-PTAA (Suzuki coupling followed by C-N coupling polymerization) is modified to prepare a block copolymer consisting of PF and PTAA functionalized with green emitting phonoxxazine moiety at the junction point of two blocks. Phenoxadine derivatives are known as a emitting dye \cite{11,12}, and have been utilized as the componet of EL copolymers \cite{13,14}. EL characteristics were preliminarily investigated for the comparison with random copolymer.
3.2 Experimental

3.2.1 Materials

Figure 3-1. illustrates the synthetic route of targeted polymers. n-Butylphenylphenoxazine \(^{(1)}\) \(^{[14]}\), 2,7-dibromo-9-(4-methylphenyl)-9-(4-octylphenyl)-fluorene \(^{(4)}\) \(^{[9]}\), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(4-methylphenyl)-9-(4-octylphenyl) fluorene \(^{(5)}\) \(^{[9]}\), 4-(4′-bromophenyl)-4′′-butyl-diphenyl amine \(^{(6)}\) \(^{[15]}\) were synthesized according to reported procedures.

All regents and solvents were used without further purification unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium and benzophenone, and stored under nitrogen atmosphere. Toluene was distilled over calcium hydrine, and stored under nitrogen atmosphere. The other regents and solvents were obtained commercially and were used as received.

3.2.2 Characterization

\(^1\)H and \(^{13}\)C NMR spectra were obtained on a JEOL ALPHA300 instrument at 25 °C at 300, and 75 MHz, respectively. Deuterated chloroform was used as a solvent with tetramethylsilane as an internal standard. Number- and weight-average molecular
weights \( (M_n \text{ and } M_w) \) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) analysis calibrated by standard polystyrene samples with a JASCO RI-2031 detector eluted with chloroform at a flow rate of 0.5 ml/min at room temperature. Differential scanning calorimetry (DSC) analysis was performed on a Rigaku DSC-8230 under nitrogen atmosphere at heating and cooling rates of 10 °C/min. UV-vis absorption spectra were obtained on a JASCO V-570 spectrophotometer and fluorescence spectra were obtained with JASCO FP-6500 spectrophotometer with an excitation at 380 nm. Cyclic voltammetry (CV) was conducted on a Niko Keisoku Model NPGFZ-2501-A potentiogalvanostat. All measurements were carried out at room temperature in a typical three-electrode cell with a working electrode (glassy carbon electrode), a reference electrode (Ag/AgCl), and a counter electrode (Pt wire) at a scanning rate of 0.1 V/s. In all measurements, acetonitrile and tetrabutylammonium tetrafluorcarbonate \((\text{Bu}_4\text{NBF}_4)\) (0.1 M) were used as a solvent and a supporting electrolyte, respectively.

### 3.2.3 Synthesis of 2,7-dibromofluorene.

Fluorene (16.62 g, 0.10 mol), 2,6-\(t\)-butyl-4-cresol (0.04 g, 0.182 mmol), \(\text{FeCl}_3\) (0.4010 g, 2.48 mmol), and chloroform (300 mL) were added into a 500-mL flask under nitrogen atmosphere and cooled down to -78 °C, and then bromine (12.5 mL, 0.244 mmol) was added dropwise slowly. After reaction for 24 h at rt, \(\text{NaHSO}_3\) aq. (300 mL) was added. The product was extracted with chloroform and dichloromethane, and the organic layer was dried with \(\text{MgSO}_4\). After the organic layer was concentrated by rotary
evaporator, the crude product was recrystallized from methanol once or twice. White crystal (26.64 g in total) was obtained. The yield was 82%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 7.68(s, 2H); 7.60(d, 2H); 7.52(d, 2H); 3.87(s, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$(ppm): 147.69, 147.37, 141.98, 130.97, 130.69, 128.76, 128.45, 121.42, 121.01, 120.37, 37.02.

3.2.4 Synthesis of 2,7-dibromofluoren-9-one.

To a 500-mL flask equipped with a stopcock were added 1 (20.0 g, 61.7 mmol) and acetic acid (150 mL) under nitrogen atmosphere. A solution of CrO$_3$ (15 g, 150 mmol) dissolved in acetic acid (120 mL) was added. After reaction for 24 h at rt, the solution was neutralized with sodium bicarbonate aq. and the precipitate was filtrated. The crude product was recrystallized from ethanol and chloroform twice. Yellow crystal (10.02 g in total) was obtained. The yield was 48%. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 7.72(d, 2H); 7.60(dd, 1H); 7.35(d, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$(ppm): 191.37, 142.28, 137.57, 135.30, 127.88, 123.42, 121.96. HR-MS(m/z): calcd for C$_{13}$H$_7$Br$_2$O, 336.8864; found, 336.8864 [M+H]$^+$.

3.2.5 Synthesis of 2,7-dibromo-9-(4-octylphenyl)fluoren-9-ol.

To a 100-mL flask equipped with a stopcock and a condenser were placed Mg (0.28 g, 12.0 mmol), 1,2-dibromoethane (0.020 mL, 0.23 mmol), and THF (2.0 mL) under nitrogen atmosphere. When Mg began to react, a solution of 4-bromooctylbenzene (3.0 g, 11 mmol) dissolved in THF (2.0 mL) was added, and the mixture was refluxed until Mg reacted completely. The solution was cooled down to rt, and then THF (37 mL) and 2 (2.80 g, 8.3 mmol) were added and the mixture was
refluxed for 16 h. After cooling, the mixture was treated with saturated NH₄Cl aq., extracted with diethyl ether. The organic layer was washed with brine, dried with MgSO₄, and concentrated by a rotary evaporator. The crude product was purified by column chromatography (chloroform : hexane = 1:1). White solid was obtained. The yield was 2.35 g (54%). ¹H NMR (300 MHz, CDCl₃) δ(ppm): 7.49(s, 4H); 7.45(s, 2H); 7.25 (d, 2H); 7.11(d, 2H); 2.56(t, 2H); 2.49(s, 1H); 1.58(m, 2H); 1.27(m, 10H); 0.87(t, 3H). ¹³C NMR (75 MHz, CDCl₃) δ(ppm): 171.43, 152.27, 142.70, 138.93, 137.57, 132.42, 128.64, 128.42, 125.23, 122.58, 121.61, 83.37, 77.58, 77.16, 76.74, 60.59, 35.74, 32.00, 31.51, 29.55, 29.37, 22.80, 21.14, 14.26. HR-MS(m/z): calcd for C₂₇H₂₈Br₂O, 526.0507; found, 526.0549[M]⁺

3.2.6 Synthesis of 2,7-dibromo-9-(4-methylphenyl)-9-(4-octylphenyl)fluorene.

To a 50-mL flask equipped with a stopcock were placed 3 (2.00 g, 3.92 mmol) and distilled toluene (48 mL) under nitrogen atmosphere, heated up to 60 °C. After trifluoromethanesulfonic acid (0.68 mL, 7.75 mmol) was added, the mixture was stirred for 2 h. The solution was neutralized with sodium bicarbonate aq., extracted with ethyl acetate, and the organic layer was dried with MgSO₄. After ethyl acetate was removed by rotary evaporator, the crude product was purified by column chromatography (hexane : ethyl acetate = 30:1). White solid was obtained. The yield was 1.91 g (83%). ¹H NMR (300 MHz, CDCl₃) δ(ppm): 7.57(d, 2H); 7.48(d, 2H); 7.46 (s, 2H); 7.04(m, 8H); 2.55(t, 2H); 2.31(s, 3H); 1.55(m, 2H); 1.27(m, 10H); 0.87(t, 3H). ¹³C NMR (75 MHz, CDCl₃) δ(ppm): 153.51, 142.00, 141.70, 138.14, 136.91, 130.91, 129.52, 129.33, 128.62, 127.95, 121.93, 121.64, 77.59, 77.16, 76.74, 65.19, 35.67, 32.03, 31.51, 29.39, 22.83, 21.11, 14.28. HR-MS(m/z): calcd for C₃₄H₃₄Br₂. 600.1027; found,
3.2.7 Synthesis of $2,7$-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(4-methylphenyl)-9-(4-octylphenyl)fluorene.

A solution of 4 (0.903 g, 1.5 mmol) dissolved in 10 mL of THF was added to a flask equipped with a stopcock under nitrogen atmosphere, and cooled to $-78$ °C. Then, $n$-butyllithium (1.34 mL, 2.6 M solution in hexane) was added dropwise, and the mixture was stirred for 30 min. To this mixture, 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.674 g, 9.0 mmol) was added, and the mixture was stirred for 12 h. The reaction mixture was quenched with brine, and extracted with diethyl ether. The organic layer was washed with brine, dried with MgSO$_4$, and concentrated by rotary evaporator. The crude product was purified by column chromatography on silica gel with hexane : ethyl acetate = 10:1 as an eluent. The white solid was obtained. The yield was 0.41 g (39%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm): 7.81(d, 4H); 7.77(d, 2H); 7.11(dd, 4H); 7.01(dd, 4H); 2.25(s, 3H); 1.55(m, 2H); 1.31(m, 24H); 1.28(m, 10H); 0.87(m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$(ppm): 151.63, 143.02, 142.96, 142.89, 141.08, 135.98, 134.26, 132.46, 128.94, 128.47, 128.23, 119.89, 83.80, 77.58, 77.16, 76.74, 65.01, 35.68, 32.05, 31.53, 29.64, 25.04, 22.82, 21.09, 14.28. Anal calcd for C$_{46}$H$_{55}$B$_2$O$_4$: C, 78.24,H, 7.08; found: C78.07, H, 6.80.

3.2.8 Synthesis of 3,7-dibromo-N-butylphenyl-phenoxazine (2).

To a 100-mL flask equipped with a stopcock and a condenser were placed N-butylphenylphenoxazine (1) (0.44 g, 1.39 mmol), chloroform (20 mL), acetic acid
(20 mL), N-bromosuccinimide (NBS) (0.52 g, 2.91 mmol) in 0°C and, the mixture was stirred for 10 h. After the reaction the solution extracted with chloroform, and organic layer washed with water and dried with MgSO₄. After chloroform was removed by a rotary evaporator, the crude product was purified by recrystallization with hexane. Light yellow solid was obtained. The yield was 0.49 g (75.0 %). \(^1\)H NMR (300 MHz, CDCl₃) \(\delta (ppm)\): 0.95 (t, 3H), 1.4 (m, 2H), 1.70 (m, 2H), 2.75 (t, 2H), 5.68 (d, 2H), 5.75 (d, 2H), 6.79 (s, 2H), 7.16 (d, 2H), 7.38 (d, 2H). \(^{13}\)C NMR (75 MHz, CDCl₃) \(\delta (ppm)\): 14.0, 22.4, 33.5, 35.4, 112.6, 114.4, 118.5, 126.2, 129.9, 131.2, 133.4, 135.4, 143.9, 144.1.

3.2.9 Synthesis of mono bromo phenoxazine (3).

To a 50-mL flask equipped with a stopcock were placed phenoxazine (1.00 g, 5.50 mmol) and distilled THF (20 mL). THF solution (15 mL) of NBS (0.97 g, 5.5 mmol) was added dropwise to the mixture and stirred for 1 h. After the filtration and the evaporation of THF, the product was resolved in ethyl acetate and washed with water 3 times. After dried with MgSO₄, and solvent was removed with a rotary-evaporator. The crude product was purified by column chromatography on silica gel with hexane : ethyl acetate = 1:1 as an eluent. The yield was 0.62 g (42%). \(^1\)H NMR (300 MHz, CDCl₃) \(\delta (ppm)\): 6.66-6.81 (m, 7H)

3.2.10 Synthesis of PF-ran-PPh (PF2, 0.2 %).

To a 10-mL flask equipped with a stopcock and a condenser were placed 4 (0.499 g, 0.143 mmol), 5 (0.500 g, 0.143 mmol), 2 (0.001 g, 0.00028 mmol), Pd(PPh₃)₄ (1 mol%),
K₂CO₃ (2 M, 2 mL) and toluene (3 mL) under nitrogen atmosphere. The mixture was heated up to 90 °C for 24 h. After the reaction the product was extracted by chloroform and washed with water and the organic layer was dried with MgSO₄. Solvent was removed with a rotary-evaporator. The crude product was purified by reprecipitation into methanol and Soxhlet extraction with acetone. The yield was 0.126 g (97%). PF2 with 8 mol% of 2 was synthesized with a similar manner (98%).

3.2.11 Synthesis of PF with phenoxazine moieties at chain end (PF1).

To a 20-mL three-necked round-bottom flask equipped with a stopcock and a condenser were added 4 (0.166 g, 0.2757 mmol), 5 (0.226 g, 0.323 mmol), Pd (PPh₃)₄ (3.46 mg, 0.003 mmol, 0.5 mol%), K₂CO₃ (2 M, 2 mL), and toluene (4 mL) under nitrogen atmosphere, and the mixture was refluxed for 48 h. Then, 3 (0.078 g, 0.3 mmol) was added and the reflux was continued for 12 h. After the reaction the product was extracted with chloroform, and washed with sat. NaCl and water. Then the organic layer was dried with MgSO₄. After the removal of the solvents, the product was obtained by precipitation into methanol. The yield was 0.20 g (79%). ¹H NMR (300 MHz, CDCl₃) δ(ppm): 0.83-0.88 (m, 3H), 1.24-1.28 (m, 10 H), 1.50-1.61 (m, 2H), 2.19-2.34 (m, 3H), 2.51-2.56 (m, 2H), 6.63-6.67 (m, 14H), 7.02-7.18 (m, 8H), 7.41-7.65 (m, 4H), 7.67-7.81 (m, 2H).
3.2.12 Synthesis of block copolymer with phenoxazine moiety at the junction (PF-Ph-PTAA).

To a 10-mL two-necked round-bottom flask equipped with a stopcock and a condenser were added PF1 (0.131 g, 0.01 mmol of the terminal), 8 (0.114 g, 0.3 mmol), P(t-Bu)_3 (7.5 µL, 0.01 mmol), Pd(OAc)_2 (0.0014 g, 0.006 mmol), t-BuONa (0.032 g, 0.33 mmol), and THF (3 mL) under nitrogen atmosphere and the mixture was stirred under reflux for 24 h. After removing the solvent by a rotary evaporator, the product was obtained by precipitation into methanol and acetone. The yield was 0.191 g (60%).

![Synthetic scheme of block and random copolymers](image)

**Figure 3-1. Synthetic scheme of block and random copolymers**
3.2.13 Device fabrication

Prior to preparation of device, a glass slide with indium tin oxide (ITO) patterns was washed by an alkaline cleaner under sonication and rinsed with deionized water. The substrate was subsequently washed by 2-propanol under sonication, and rinsed with clean 2-propanol, and dried with nitrogen. PEDOT:PSS with 30 nm of thickness was spin-coated on the substrate at 2500 rpm for 30 s from the dispersion in water filtered by 0.2 μm of membrane filter followed by annealing at 200 °C for 1 h. Polymer layer was laminated on PEDOT:PSS by spin-coating at 500 rpm for 30 s from chlorobenzene solution (12 mg/mL) filtered by 0.45 μm of membrane filter, and annealed at 120 °C for 1 h under nitrogen atmosphere. On the polymer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) with 50 nm thickness was deposited by thermally evaporation in carbon pot at 240 °C under vacuum with a rate of 1.5 Å/s. As a cathode, lithium fluoride with 0.5 nm of thickness followed by a Al with 100 nm of thickness was deposited on the organic layer with a rate of 0.1 Å/s and a rate of 4.5 Å/s using tantalum and tungsten boats, respectively. Finally the polymer device was set into a metal can with barium oxide as a drying agent under a nitrogen atmosphere, and passivated with an epoxy resin (XNR 5570-B1, Nagase chemtex Corporation) irradiated by UV light.
3.3 Result and discussion

3.3.1 Synthesis

In order to prepare the PF homopolymer with phenoxadine moieties (PF1 in Figure 3-1), Suzuki coupling polymerization of 4 and 5 in non-stoichiometric conditions (4/5 = 0.85/1.0) was carried out resulting in an end-functional polymer with boronic ester moieties, followed by the reaction with monobrominated phenoxazine. The successful introduction of phenoxazine moieties was confirmed by $^1$H-NMR spectrum. As shown in Figure 3-2a, signals for phenoxazine protons appeared around 6.6 ppm. In order to obtain a target block copolymer (PF-Ph-PTAA) consisting of PF and PTAA functionalized with green emitting phenoxazine moiety at the junction point of two blocks, C-N coupling polymerization of 6 was conducted in the presence of PF1 using palladium acetate and tri(tert-butyl)phosphine ligand, and tert-butoxide as a base in THF for 24 h in the similar manner we reported $^{[9, 15]}$. As shown in Figure 3-2b, two types of methyl signals around 0.85 ppm, and N-H signal from polymer ends (5.7 ppm) were observed indicating the introduction of TAA unit as expected.
Figure 3-2. $^1$H-NMR of synthesized polymers measured in CDCl3 at 500MHz and 25°C.
Figure 3-3 shows GPC profiles for PF1 and PF-Ph-PTAA. GPC trace of PF-Ph-PTAA was monomodal and shifted toward the higher molecular weight direction compared with PF1 homopolymer. Both NMR and GPC results suggest the successful formation of the designed block copolymer. Random copolymers, PF2s, were also synthesized by Suzuki coupling polymerization of 2 and 4 with 5. Table3-1 lists the characteristics of prepared polymers together with the data for PF-b-PTAA, which is a previously prepared block copolymer without phenoxazine units\(^{[9,10]}\).

Glass transition temperature of PF-Ph-PTAA was determined to be 148°C by DSC, and this value is almost the same as that of PF-b-PTAA. All the polymers were soluble in common organic solvents and readily formed thin films by a solution processing.

![Figure 3-3. GPC profiles of PF1 and PF-Ph-PTAA. Effluent was monitored with UV detector (254 nm)](image-url)
Table 3-1. Characteristics of synthesized polymers

<table>
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<tr>
<th>polymer</th>
<th>Mn/10&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;a&lt;/sup&gt;</th>
<th>FL content&lt;sup&gt;b&lt;/sup&gt; (mol%)</th>
<th>Phenoxazine content (mol%)</th>
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</thead>
<tbody>
<tr>
<td>PF1</td>
<td>4.1</td>
<td>4.0</td>
<td>78</td>
<td>22</td>
</tr>
<tr>
<td>PF-Ph-PTAA</td>
<td>11</td>
<td>3.4</td>
<td>44</td>
<td>13</td>
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<tr>
<td>PF2 (0.2%)</td>
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<td>2.4</td>
<td>99</td>
<td>0.2</td>
</tr>
<tr>
<td>PF2 (8%)</td>
<td>25</td>
<td>3.2</td>
<td>92</td>
<td>8.0</td>
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<tr>
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<td>19</td>
<td>2.4</td>
<td>57</td>
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</table>

<sup>a</sup> determined by GPC, <sup>b</sup> determined by <sup>1</sup>H-NMR, <sup>c</sup> Ref. [10]

3.3.2 Optical and electrochemical properties

The optical properties of prepared polymers were investigated with UV-vis absorption and photoluminescent (PL) spectroscopies. In chloroform solutions, all polymers we examined possess similar optical properties regardless of the existence of phenoxazine moiety as shown in Table 3-2. In a solution state, all copolymers showed λ<sub>abs, max</sub> of 382-385 nm, and exhibited similar PL spectra in solution state, having distinct vibronic bands at about 418 and 445 nm and a shoulder around 470 nm upon excitation at 380 nm. As we previously reported<sup>[9,10]</sup>, PTAA segments show negligible contribution to PL spectrum. It is also found that phenoxazine units existing at the junction point, or in the fluorene sequence of random copolymers also have almost no
effects on the UV and PL spectra in the solution state.

**Figure 3-4** shows UV-vis (a) and PL (b) spectra in a film state. Only PF2(8%) showed different absorption spectrum as shown in **Fig. 3-4a**. The observation of a tail over 420 nm is probably due to the interchain interaction between phenoxazine rich sequences. The existence of phenoxazine significantly influenced PL spectra in the film state (**Fig. 3-4b**). PF-b-PTAA shows similar PL spectrum to that of solution indicating that interchain interaction is negligible because of the bulky substituent. However, only 0.2% of phenoxazine moiety drastically changed the PL spectrum, *i.e.*, the spectrum showed emission peaks at 426, and 450 nm with a tail. In the case of PF2(8%), further red shift was observed showing emission maximum only at 463 nm, indicating the effective energy transfer. Although the content of phenoxazine unit in PF-Ph-PTAA was relatively high (17%) as a result of the low molecular weight nature, it showed similar PL spectrum to that of PF2(0.2%). This is because phenoxazine unit is isolated in single polymer chain nevertheless the high content, and/or microphase separated structure is established in PF-Ph-PTAA film.

The electrochemical properties of the copolymers were investigated by cyclic voltammetry (CV) with a reference electrode of Ag/AgCl. The oxidation process of PF-Ph-PTAA started around 0.84 V, and the reversible redox peak in the reduction process appeared at around -0.71 V. The energy levels of the highest occupied molecular orbital (HOMO) of the PF-Ph-PTPA was estimated from its oxidation potential according to an empirical formula, $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4)$ V. HOMO level of the block
copolymer was in -5.24 eV. The levels of the lowest unoccupied molecular orbital (LUMO) for the polymer were calculated with the reduction potential $E_{\text{red}}$ from the empirical formula $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.4) \text{ V}$. LUMO level of the block copolymer was in -3.69 eV. This result was almost consistent with that of PF-b-PTAA\(^{[10]}\).

![Figure 3-4. UV-vis (a) and PL (b) spectra of synthesized polymers in a film state.](image)

Excitation wavelength; 380 nm.
### Table 3-2. Optical properties of synthesized polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>( \lambda_{\text{max} ,(\text{UV})} / \text{nm} )</th>
<th>( \lambda_{\text{max} ,(\text{PL})}^a / \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solution(^b)</td>
<td>film</td>
</tr>
<tr>
<td>PF-Ph-PTAA</td>
<td>382</td>
<td>380</td>
</tr>
<tr>
<td>PF2 (0.2%)</td>
<td>385</td>
<td>380</td>
</tr>
<tr>
<td>PF2 (8%)</td>
<td>385</td>
<td>380</td>
</tr>
<tr>
<td>PF-b-PTAA</td>
<td>385</td>
<td>385</td>
</tr>
</tbody>
</table>

\(^a\) exited at 380 nm, \(^b\) CHCl\(_3\) solution, 10\(^{-2}\) mg/mL, \(^c\) 10\(^{-4}\) mg/mL

### 3.3.3 EL properties

The performance of the EL devices based on **PF-Ph-PTAA** with the device structure of ITO/PEDOT:PSS/polymer/LiF/Al was evaluated. The device with PF-Ph-PTAA blended with 20 wt% of PF-b-PTAA was also evaluated in order to elucidate the chemical environment where phenoxazine moiety locates. **Figure 3-5** showed luminance vs. voltage (a), and current efficiency vs current density (b) characteristics, respectively. Although the maximum luminance for the device based on PF-Ph-PTPA with 20 wt% of PF-b-PTPA (1710 cd/cm\(^2\)) is slightly higher than neat PF-Ph-PTPA, both devices afforded the similar current efficiency profiles. As discussed in PL section, phenoxazine unit is isolated in single polymer chain nevertheless the high content. Therefore, the environment of emitting centers in both devices is similar each
other. Compared with the device based on PF-b-PTAA \textsuperscript{[10]}, EL performance is slightly worse. It is speculated that this is due to the low molecular weight nature of PF-Ph-PTAA, which results in the unclear microphase separation.

**Figure 3-6** shows EL spectra for fabricated devices. Compared with the device based on PF-b-PTAA, all the devices based on phenoxazine containing polymers show ca. 50 nm red-shift. It is indicated that emission sites predominantly located in the vicinity of phenoxazine moiety. Because of shallow HOMO level of phenoxazine unit \textsuperscript{[14]}, it works as a hole trap resulting in the efficient recombination of hole and electron. Contrary to PL spectra, PF-Ph-PTAA showed similar EL spectrum to PF2(8%), where a tail was observed in the long wavelength region. It is possible that the interaction of excitons exists because of the local high concentration of phenoxazine moiety.
Figure 3-5. EL characteristics of device based on PF-Ph-PTAA (circle) and PF-Ph-PTAA + 20 wt% of PF-b-PTAA (triangle). a) luminance vs. voltage, b) current efficiency vs current density.

Figure 3-6. Electroluminescent spectra for devices based on synthesized polymers obtained at 10 V.
3.4 Conclusions

A block copolymer consisting of electron transporting PF and hole transporting PTAA functionalized with green emitting phenoxazine moiety at the junction point of two blocks was successfully prepared via the combination of Suzuki and C-N coupling polymerization based on the novel molecular design of full functional polymers for the increase the efficiency in PLED. Prepared polymers exhibited similar optical properties in chloroform solutions. On the other hand, in a film state, the existence of phenoxazine unit drastically changed PL spectra. Although the content of phenoxazine unit in PF-Ph-PTAA was relatively high (13 %), it showed similar PL spectrum to that of PF2 (0.2 %) indicating that phenoxazine unit is isolated in single polymer chain nevertheless the high content. EL device based on PF-Ph-PTAA showed green-emission, suggesting that emission sites predominantly located in the vicinity of phenoxazine moiety because of its shallow HOMO level. Our molecular design presented here makes it possible to control the emission site, and to afford more efficient materials for EL applications
3.5 References


Chapter 4. Polyfluorene-polytriarylamine block copolymer as an additive for electroluminescent devices based on polymer blends

4-1 Introduction

The first Polymeric light-emitting diodes (PLED) based on the electroluminescence of poly(p-phenylenevinylene) (PPV) was reported by Cambridge University in 1990 [1]. From then on, PLED have attracted great attention due to their potential applications in full-color, large-area, paper-thin flexible displays and so on. Green-, red- and white-light-emitting materials are generally prepared by introducing appropriate doping components into bulk-emitting materials [2]. Therefore, developing efficient, stable and deep blue PLED is essential.

A large number of photoactive and electro-conjugated polymers have been introduced for PLED applications in recent decades, such as poly(p-phenylenevinylene) (PPV) [3,4], polythiophene (PT) [5] and polyfluorene (PF) [6-8]. Incorporating some functional components such as charge transport or luminescent moieties into active layer can easily adjust the charge balance in polymer EL devices. Numerous works fabricating device with polymer blend [9-12] and random copolymer [13,14] have been reported in order to improve injection of hole and electron into active layer as well as
recombination of charges and to introduce function side groups. Furthermore, multilayer blue emitting EL device based on fluorene-triarylamine alternating copolymer showed a high current efficiency as 8.7cd/A\textsuperscript{[15]}. Moreover, we demonstrated that the device based on bipolar charge transporting block copolymers showed higher current efficiency compared with random copolymers or polymer blends with the same composition\textsuperscript{[16-18]}.

In our previous work, it was found that polyfluorene-\textit{b}-polytriphenylamine (PF-PTPA) block copolymer showed better device performance than that of corresponding PF homopolymers due to the incorporation of hole transporting PTPA segments into PF backbone to offer the effective charge recombination\textsuperscript{[19]}. In this work, we performed further investigation on device performance based on polymer blend systems (PF-PTPA/PF and PF-PTPA/PF/PTPA), to which various contents of PF-PTPA block copolymer were added.

**4-2 Experimental**

**4-2-1 Materials**

Toluene was distilled over calcium hydride and stored under nitrogen. Tetrahydrofuran (THF) was used as distilled over sodium and benzophenone.
As reported in the previous work \cite{19}, homopolymers PF1, PF2 were prepared via Suzuki coupling polymerization from monomers 2,7-dibromo-9-(4-methylphenyl)-9-(4-octylphenyl)fluorene and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(4-methylphenyl)-9-(4-octylphenyl)fluorene followed by terminal modification with (4′-bromobiphenyl-4-yl)-(4-{2-[2-(methoxyethoxy)ethoxy]ethoxy}phenyl)amine (monomer 1), homopolymer PTPA as well as block copolymer PF-PTPA1, PF-PTPA2 were prepared via C-N coupling polymerization initiated by 1 under nitrogen atmosphere. The other reagents were used as received without further purification.

4-2-2 Device fabrication

Prior to preparation of device, a glass slide with indium tin oxide (ITO) patterns was washed by an alkaline cleaner under sonication and rinsed with deionized water. The substrate was subsequently washed by 2-propanol under sonication, rinsed with clean 2-propanol, and dried with nitrogen. PEDOT:PSS with 30 nm of thickness was spin-coated on the substrate at 2500 rpm for 30 s from the dispersion in water filtered by 0.2 μm of membrane filter, followed by annealing at 200 °C for 1 h. Polymer layer was laminated on PEDOT:PSS by spin-coating at 500 rpm for 30 s from chlorobenzene
solution (12 mg/mL) filtered by 0.45 μm of membrane filter, and annealed at 120 °C for 1 h under nitrogen atmosphere. On the polymer, 2,9-dimethyl-4,7-di phenyl-1,10-phenanthroline (BCP) with 50 nm thickness was deposited by thermally evaporation in carbon pot at 250 °C under vacuum with a rate of 1.5 Å/s. As a cathode, lithium fluoride with 0.5 nm of thickness followed by Al with 100 nm of thickness was deposited on the organic layer with a rate of 0.1 Å/s and a rate of 4.5 Å/s using tantalum and tungsten boats, respectively. Finally, the polymer device was set into a metal can with barium oxide as a drying agent under a nitrogen atmosphere, and passivated with an epoxy resin (XNR 5570-B1, Nagase ChemteX Corporation) irradiated by UV light. The typical active area of the EL devices was 4-8 mm². The current-voltage characteristics and luminance were measured with a Keithley 2400 source meter and a Topcon BM-8, respectively.

**4-2-3 Measurements**

¹H NMR spectra were obtained on a JEOL ALPHA300 instrument at 300 MHz at 25 °C. Deuterate chloroform was used as a solvent with tetramethylsilane as an internal standard. Number- and weight-average molecular weights (M_n and M_w) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC)
analysis with a JASCO RI-2031 detector eluted with chloroform at a flow rate of 0.5 ml/min at room temperature and calibrated by standard polystyrene samples. Differential scanning calorimetry (DSC) analysis was performed on a Rigaku DSC-8230 under nitrogen atmosphere at heating and cooling rates of 10 °C/min. UV-vis absorption spectra were obtained on a JASCO V-570 spectrophotometer and fluorescence spectra were obtained with JASCO FP-6500 spectrophotometer with an excitation at 380 nm. All the polymer blend films were spincoated on a glass slide from chloroform solution. Atomic force microscopic (AFM) measurements were performed on a JEOL JSPAM 4200 system in tapping mode (phase and topographic modes) with an MPP 11100-10 silicon probe (resonant frequency: 300 KHz, force constant: 40 N/m). All thin films of polymers were spin-cast onto glass slide which was spin-casted by PSS:PEDOT before and then annealed at 120 °C for 1 h.

4-3 Results and discussion

PF homopolymers, PTPA homopolymer and PF-PTPA block copolymers were synthesized for EL application (Figure 4-1). In order to avoid the formation of aggregates/excimers and suppress interchain interactions in PF, octylphenyl and methylphenyl groups were introduced at the 9-position of fluorene, PTPA was modified
with tri(ethylene oxide) (TEO) group, which is considered to predominantly interact with hydrophilic PEDOT/PSS layer in EL device to prevent the migration of an impurity from PEDOT/PSS layer to PF emitting layer by the formation of poly(triphenylamine) skin layer between them.

Figure 4-1. Chemical structure of PTPA, PF and PF-PTPA.

Various molar ratio of bromo-group/boronic-ester-group to 0.92/1.08 and
0.98/1.02, PF 1 and PF 2 were prepared via Suzuki coupling reaction. The number average molecular weights ($M_n$) of PF 1 and PF 2 estimated by GPC were 13400 and 26400 with a molecular-weight dispersity ($M_w/M_n$) of 2.42 and 3.48, respectively. C-N coupling polymerization in the presence of the PF 1, 2 provided PF-\textit{block}-PTPA-\textit{block}-PF triblock copolymers PF-PTPA 1, 2 \textsuperscript{[20]}. The molar ratio of PF and PTPA repeating units ($N_{PF}/N_{PTPA}$) for PF-PTPA 1 and 2 was determined as 6/5 and 6/4 by $^1$H NMR spectra, respectively, depending on the area integral of ether proton and aliphatic proton. According to the previous report \textsuperscript{[19]}, the device based on the block copolymer with the composition ratios of above showed nearly the highest current efficiency, while PF homopolymers with different molecular weights existed similar device performance. The homopolymers, PF 1 and PF 2, showed $T_g$ of 118 and 119 °C, respectively. PTPA homopolymer exhibited relatively high $T_g$ of 175 °C. PF-PTPA2 showed two distinct transitions at 119 and 173 °C, corresponding to $T_g$s of PF and PTPA, respectively, which indicate the microphase separated structure. Another block copolymer, PF-PTPA 1, also showed double $T_g$s.
Table 4-1. Characterizations of PF-PTPA block copolymer.

<table>
<thead>
<tr>
<th>Molar ratio 1/2</th>
<th>Molar ratio(^{a}) of PF/PTPA (in polymer)</th>
<th>(M_n^{b})</th>
<th>PDI(^{b})</th>
<th>Yield (%)</th>
<th>(T_g) (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF 1 0.92/1.08</td>
<td>-</td>
<td>13400</td>
<td>2.42</td>
<td>83</td>
<td>118</td>
</tr>
<tr>
<td>PF-PTPA 1</td>
<td>6/5</td>
<td>23100</td>
<td>2.67</td>
<td>48</td>
<td>118, 174</td>
</tr>
<tr>
<td>PF 2 0.98/1.02</td>
<td>-</td>
<td>26400</td>
<td>3.48</td>
<td>85</td>
<td>119</td>
</tr>
<tr>
<td>PF-PTPA 2</td>
<td>6/4</td>
<td>43400</td>
<td>3.28</td>
<td>47</td>
<td>119, 173</td>
</tr>
<tr>
<td>PTPA</td>
<td>-</td>
<td>9700</td>
<td>2.80</td>
<td>94</td>
<td>175</td>
</tr>
</tbody>
</table>

\(^{a}\) : Determined by \(^{1}\)H NMR spectra \quad \(^{b}\) : Determined by GPC

A series of EL devices based on PF-PTPA1/PF1 blend system (with the weight ratio of PF-PTPA6 block copolymer as 100 wt%, 77 wt%, 62 wt%, 45 wt%, 27 wt% and 0 wt% or the molar ratio of (PF-PTPA)/PF as (6/5)/0, (6/5)/3, (6/5)/6, (6/5)/12, (6/5)/24 and 0/1) with the configuration of ITO/PEDOT:PSS(30 nm)/polymer(30 nm)/BCP(50nm)/LiF(0.5nm)/Al(100 nm) on the glass substrate were prepared, and the device performances were characterized. Figure 4-2 showed current efficiency – current density characteristics. The EL characteristics were summarized in Table 4-2.
Figure 4-2. Current efficiency- current density characteristics for the devices based on PF1/PF-b-PTPA1 blend systems.

Table 4-2. EL characteristics for the devices based on PF1/PF-b-PTPA1 blend systems.

<table>
<thead>
<tr>
<th>Weight ratio of block</th>
<th>Molar ratio of (PF-PTPA)/PF</th>
<th>Luminance at 30 mA/cm$^2$ (cd/m$^2$)</th>
<th>Maximum luminance (cd/m$^2$)</th>
<th>Maximum current efficiency (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Block1</td>
<td>(6/5)/0</td>
<td>626</td>
<td>2230</td>
<td>2.10 (14V)</td>
</tr>
<tr>
<td>Block1/PF1 (77 wt%)</td>
<td>(6/5)/3</td>
<td>648</td>
<td>2461</td>
<td>2.12 (15V)</td>
</tr>
<tr>
<td>Block1/PF1 (62 wt%)</td>
<td>(6/5)/6</td>
<td>547</td>
<td>2378</td>
<td>1.91 (15V)</td>
</tr>
<tr>
<td>Block1/PF1 (45 wt%)</td>
<td>(6/5)/12</td>
<td>443</td>
<td>2032</td>
<td>1.63 (15.5V)</td>
</tr>
<tr>
<td>Block1/PF1 (27 wt%)</td>
<td>(6/5)/24</td>
<td>328</td>
<td>1573</td>
<td>1.25 (16V)</td>
</tr>
<tr>
<td>PF1</td>
<td>0/1</td>
<td>297</td>
<td>1164</td>
<td>1.07 (13V)</td>
</tr>
</tbody>
</table>

The luminescence intensities based on all the blend systems were exponentially
increased with an increase in voltage. At the similar current density (for example, 30 mA/cm²), with increasing the weight ratio of block 1, PF-PTPA1/PF1 (100wt%, 77wt%, 62wt%, 45wt%, 27wt% and 0wt%) blend systems showed higher luminance (626, 648, 547, 443, 328 and 297 cd/m²). Moreover, similar results were obtained for the maximum luminance. The maximum current efficiencies of PF-PTPA1/PF1 blend systems were from 1.07 to 2.12 cd/A. Adding 27wt% of block 1, the current efficiency was almost coincident with that of the block-only device, reaching to 2.12 cd/A in the maximum. However, decreasing the amount of block 1, the device performance decreased subsequently. Device based on PF homopolymer (PF-PTPA 0wt%) showed the lowest current efficiency and luminance. Existence of block copolymer in polymer blend generally improved an efficient hole injection, due to the attachment of PTPA segment to PF backbone. There was critical point (less than 27 wt%) where the current efficiency drastically changed (Figure 4-5), although most of the systems have the same composition of hole and electron transporting unit. Suitable proportion of block copolymer and PF homopolymer in blend system maybe provided more balance between hole and electron charges in the emitting layer.

Figure 4-3 showed current efficiency – current density characteristics for the PF-PTPA2 / PF2 / PTPA blend systems. The EL characteristics were summarized in Table 4-3. Although it is found that the addition of PTAA component to the active layer by improved the performance as shown in Figure 4-2 and Table 4-2, the simple blend of both homopolymers afforded the worst performance we examined.
This result strongly suggests that the morphology in the active layer also plays an important role as well as its chemical characters. In fact the maximum current efficiency and luminescence at 30 mA/cm² increased with the increase of the content of PF-b-PTAA2. The similar effect of a block copolymer as an additive was observed for electro-phosphorescent devices based on the blend systems consisting of two types of vinyl homopolymers (hole and electron transporting), and bipolar block copolymer with both segments.\textsuperscript{[18]}

\textbf{Figure 4-3.} Current efficiency- current density characteristics for the devices based on PF2/PTPA/PF-b-PTPA2 blend systems.
Table 4-3. EL characteristics for the devices based on PF2/PTPA/PF-b-PTPA2 blend systems

<table>
<thead>
<tr>
<th>Weight ratio of block</th>
<th>Molar ratio of (PF-PTPA)/PF/PTPA</th>
<th>Luminance at 30 mA/cm² (cd/m²)</th>
<th>Maximum luminance (cd/m²)</th>
<th>Maximum current efficiency (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Block2</td>
<td>(6/4)/0/0</td>
<td>724</td>
<td>2350</td>
<td>2.15 (15V)</td>
</tr>
<tr>
<td>Block2/PF2/PTPA (80 wt%)</td>
<td>(6/4)/1.5/1</td>
<td>648</td>
<td>2619</td>
<td>2.28 (16.5V)</td>
</tr>
<tr>
<td>Block2/PF2/PTPA (60 wt%)</td>
<td>(6/4)/4/2.7</td>
<td>521</td>
<td>2256</td>
<td>2.07 (16V)</td>
</tr>
<tr>
<td>Block2/PF2/PTPA (40 wt%)</td>
<td>(6/4)/9/6</td>
<td>478</td>
<td>2257</td>
<td>1.78 (17V)</td>
</tr>
<tr>
<td>Block2/PF2/PTPA (20 wt%)</td>
<td>(6/4)/24/16</td>
<td>407</td>
<td>1688</td>
<td>1.51 (17V)</td>
</tr>
<tr>
<td>PF2/PTPA</td>
<td>0/6/4</td>
<td>235</td>
<td>879</td>
<td>0.88 (14V)</td>
</tr>
</tbody>
</table>

Figure 4-4. AFM images for PF2/PTPA/PF-b-PTPA2 blend films on PEDOT/PSS (tapping mode). PF-b-PTPA2 content is a) 100 wt%, b) 80 wt%, c) 60 wt%, d) 40 wt%, e) 20 wt%, and f) 0 wt%. All thin films (ca. 30 nm thick) were annealed at 120 °C for 1 h.
Figure 4-4 represents the AFM images of blend films with the thickness of ca. 30 nm on PEDOT/PSS in a tapping mode (JEOL JSPM 4200 system). In the simple blend (Fig. 4-4 f), ca. 1 μm of domains were observed, and the domain size decreased as the content of PF-b-PTAA2 increased. These results indicate that the finer domain size was achieved by the addition of the block copolymer as expected, and was favorable for better EL performance. Higher current efficiency was observed at the higher current density region for the blend system (80 wt% of block copolymer) than block only device. As discussed above, this is probably due to the appropriate domain size for the effective recombination and/or carrier balance in the blend system.

Figure 4-5. Relationship between the content of block copolymer and EL performance. Filled and open symbols are for the devices based on PF1/PF-b-PTAA1, and PF2/PTAA/PF-b-PTAA2 blend systems, respectively. Circle and triangle represent luminescent at 30 mA/cm2 and maximum current efficiency, respectively.
The relationship between the block copolymer content and EL performance for both blend systems are shown in Figure 4-5. For both cases, the maximum current efficiencies increased with the content of the block copolymer, and reached almost constant values at 80 wt%. The addition of block copolymers altered mainly the chemical nature of the active layer in the first blend system, and changed the morphological nature in the second system. As shown in Figure 4-5, it is found that EL performance is governed by the both factors which can be controlled by the utilization of block copolymers as the additive to PF or PF/PTAA blend systems. Figure 4-6 shows EL spectra for typical two types of devices (PF1/PF-b-PTAA1 77 wt%, and PF2/PTAA/PF-b-PTAA 80 wt%). These profiles are almost the same as that observed for the block copolymer based device \cite{19}. Other devices also exhibited a similar blue EL profiles without unnecessary green-emitting bands.
4-4 Conclusions

In conclusion we demonstrated the method how to improve the EL performance of blue-emitting devices based on polymer blends. PF-b-PTAA block copolymer afforded hole injecting and/or electron blocking ability to PF, and it worked as a compatibilizer for PF/PTAA blend to control the morphology of blend films. It is necessary to investigate the effect of the molecular weights of both homopolymers and block copolymer, and the chemical composition of the latter for the optimized morphology and EL performance.

4-5 References


K. Polymer 2010, 51, 616


Chapter 5. Summary

As mentioned in Chapter 1, among the vast array of known $\pi$-conjugated polymers, polyfluorene (PF) is the most promising candidate as a blue-light-emitting and electron-transporter polymers because of excellent properties, of course, several modifications should be carried for PF to overcome their inherent disadvantages, such as formation aggregation and imbalance charge transportation, to improve the electroluminescent device performances. We introduced a kind of PBD and PTPA polymers as the electron-transporter and the hole-transporter material. PBD polymer material with oxadizole function group is a good material for electron transporting from cathode to the emitting layer because of LUMO energy level. PTPA polymer material with third kind of amine is good material for hole transporting from anode to the emitting layer. For keeping low the coast of device fabrication in the industrial applications we studied in POLEDs because they can fabricate with wet process such as spin-coating or ink-jetting. But in wet process for fabricate a device with multy layer structure because of mingling between the layers, the solvent selection is very hard job and in some cases it is impossible because of nearing solubility of materials. To solve this problem we studied on full functional block copolymer material for designing the single layer device.
The first part of this thesis (Chapter 2) deals with the synthetic methods of 2-(4-t-butylphenyl)-5-(4-vinylphenyl-4'-yl)-1,3,4-oxadiazole (PBD) and 4-(4'-Bromobiphenyl)-4''-n-butyldiphenylamine (TPA). In this method, for synthesis the block copolymer with an emitting part at the junction we designed a two functional initiator with an emitting part on it. In this initiator we designed two reaction points in the initiator. One of them is a point of aryl halide for using in Buchwald-Hartwig C-N cross coupling for synthesis the PTPA homo polymer and the other point is designed as an alkyl halide which is suitable for ATRP reaction for synthesis the block copolymer. However, few characteristic peak from the PTPA and terminal group (emitting part) was observed in \(^1\)H-NMR spectrum of PTPA homo polymer synthesized via Buchwald-Hartwig C-N coupling and characteristic peak from the PBD group was also observed in block copolymer. Block copolymer was readily soluble in common organic solvents, had good thermal stability and readily formed thin film via solution processing.

In Chapter 3, deals with the synthetic methods of 2,7-dibromo-9-(4-methylphenyl)-9-(4-octylphenyl)fluorine (PF) and 4-(4'-Bromobiphenyl)-4''-n-butyldiphenylamine (TPA). Octylphenyl and methylphenyl are introduced to the 9,9-position of fluorene to reduce the chain aggregation of polyfluorene's backbones and to improve the color stability and the long life time. Polyfluorene homopolymers were synthesized by Suzuki coupling reaction. The synthesis conditions and product characterization were handled easily by Suzuki
coupling reaction and Suzuki-Miyaura reaction. However, few characteristic peak from the terminal group (mono bromo phenoxazine) was observed in $^1$H NMR spectrum of PF homopolymer synthesized via Suzuki-Miyaura reaction. PF homopolymers were readily soluble in common organic solvents, had good thermal stability and readily formed thin film by solution processing. Even after thermal ennealing at 120°C for 120 min in air, the PF homopolymers and PF-PTPA block copolymers showed good thermal stability. PF-phenoxazine-PTPA block copolymers showed relatively high HOMO values in compare with those of PF homopolymers by cyclic voltammetry, provided a very good match to the work function of PEDOT/PSS(-52 eV), suggested facile hole injection from ITO/PEDOT/PSS into the HOMO of PF-PTPA block attached to the PF backbone. All of the polymers exhibited a similar absorption peak both in chloroform solution and in film state, while the PL emission was also observed in the range of green-light wavelength.

The unbalance between the two kinds of charges (electron transport faster than holes) in polyfluorene backbones, can cause of the low EL efficiency. As a kind of hole-transporting structure, PTPA block is attached to PF backbone to improve the charge balance. A series of electroluminescent devices based on poly fluorine-block-polytriphenylamine with phenoxazine at the junction block copolymers were fabricated, and current density (I)-voltage (V)-luminance(L) characteristics were evaluated for devices.

In the last part of this thesis, a series of electeroluminecent devices based on
polyfluorene-block-poly(triphenylamine) block copolymers and their blend system with homo PF or PTPA homopolymers were fabricated and the current density(I)-voltage (V)-luminance(L) characteristics were evaluated for devices. To verify the influence of block copolymers into the micro phase separation, the morphology of the polymers thin layers in blend systems was observed.
Achievement

Papers


2) Synthesis of Polyfluorene and Triphenylamine Block Copolymer with Emitting Part at Junction for Light Emitting Application, Mehdi Jahanfar, Kenji Ogino, accepted in *Open Journal of Organic Polymer Materials*. (Chapter 3)

3) Polyfluorene-polyphenylamine block copolymer as an additive for improvement of electroluminescent performance, Mehdi Jahanfar, Ying Tan, Kousuke Tsuchiya, Kenji Ogino, accepted in *Open Journal of Organic Polymer Materials*. (Chapter 4)