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Efficient and color pure blue light emitting random copolymer with fluorene and fluorenylstilbene

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Abstract

A blue electroluminescent polymer, random copolymer of fluorenylstilbene and fluorene, was prepared by the nickel catalyzed coupling reaction. The structure and properties of the copolymer were analyzed by various spectroscopic methods. The obtained polymer had good solubility and thermal stability with high T_g. The polymer in thin film emits strong blue luminance (max = 468 nm) with narrow bandwidth upon photoexcitation. PL spectrum of the polymer in the film is almost consistent with that of solution one as well as the EL spectrum, indicating that the aggregation and the excimer fluorescence are suppressed by the introduction of fluorenylstilbene comonomer. Moreover, the introduction of fluorenylstilbene comonomer lowered the oxidation potential to lead feasible hole injection, when the compared with poly(fluorene) homopolymer. The ITO/PEDOT/polymer/LiF/Al device showed the maximum brightness of 3500 cd/m^2 with a turn on voltage of 4.4, the maximum efficiency of 0.878 lm/W and blue emission with CIE chromaticity coordinates of ((x,y) = (0.17, 0.25)).

Keywords: Blue light emitting; Randomcopolymer; Fluorene and fluorenylstilbene

1. Introduction

Polymeric light emitting diodes have attracted tremendous attention in the past decade owing to their potential advantages such as outstanding mechanical and optical properties, low-cost manufacturing, and amenability to large area displays. Following the discovery of electroluminescence (EL) in poly(*p*-phenylenevinylene) (PPV) [1], various EL conjugated polymers have been synthesized and studied in detail [2–10]. The electroluminescence from these polymers can sweep the full range of the visible spectrum.

Amongst the variety of EL conjugated polymers, blue light emission is deemed desirable since, it is generally more difficult to fabricate such LEDs from inorganic semiconductors. Furthermore, full color exhibition and white light devices need blue light. For blue emission, conjugated polymers need to have a large bandgap and defined optical properties. Many studies on blue LEDs were done mainly on polyalkylfluorene (PDAF) [11] and poly(*p*-phenylene)s (PPPs) [2]. Especially, poly(dialkyfluorene)s (PFs) are considered by several research and industrial groups as the most promising blue light emitting material due to the chemical and thermal stability, high photoluminescence quantum efficiency and easy processability through introduction of solubilizing groups in the 9-position of the fluorene ring [12–18]. Major drawbacks of PFs, however, are that they show excimer and/or aggregate formation upon thermal annealing or the passage of current. Moreover, the efficiency of devices based on PFs is not sufficient for industrial applications. Continuing efforts have been made to suppress excimer formation and improve efficiency in PFs, including copolymerization with anthracene, end capping with a sterically hindered groups, and introducing sterically hindered substituents at the 9-position of fluorine [19–25].

It is also reported that one of the drawbacks based on polyfluorene derivatives is the injection of holes from the

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anode due to the low ionization potential (IP). The control of the ionization potential becomes important for the optimization of PLEDs made from this class of polymers.

Recently, we reported the blue light emitting materials, which are composed with having advantages of PPV and PPP. And, our group research also involved introducing bulky substituents into vinyl bridge. It is known that the formation of aggregates and interchain excimers can be suppressed by decreasing the tendency toward crystallization of the polymer chains and by increasing the glass transition temperature, thereby increasing the stability of the amorphous state in solid films. Thus, the bulky pendant groups attached to a vinyl bridge leads to enhance the solubility, and thermal and oxidative stability of resulting polymers as well as increased efficiency due to reduced intermolecular interaction and(or) excimer aggregation [26–30]. Moreover, because it is reported that PPV containing phenylene vinylene unit is feasible for hole injection [31], the introduction of stilbene can lead the low onset of the oxidation potential of the polymer, and the balance in charge carriers.

In this article, we designed the random copolymer of fluorenylstilbene and fluorene from 1,2-bis(4′-bromophenyl)-1-(9″,9″-dihexyl-3-fluorene)ethene and 2,7-dibromo-9,9-dihexylfluorene. It is expected that the obtained polymer has the high efficient blue color due to balanced charge carriers, inhibited intermoleular interaction and(or) excimer aggregation as well as good solubility and good thermal stability.

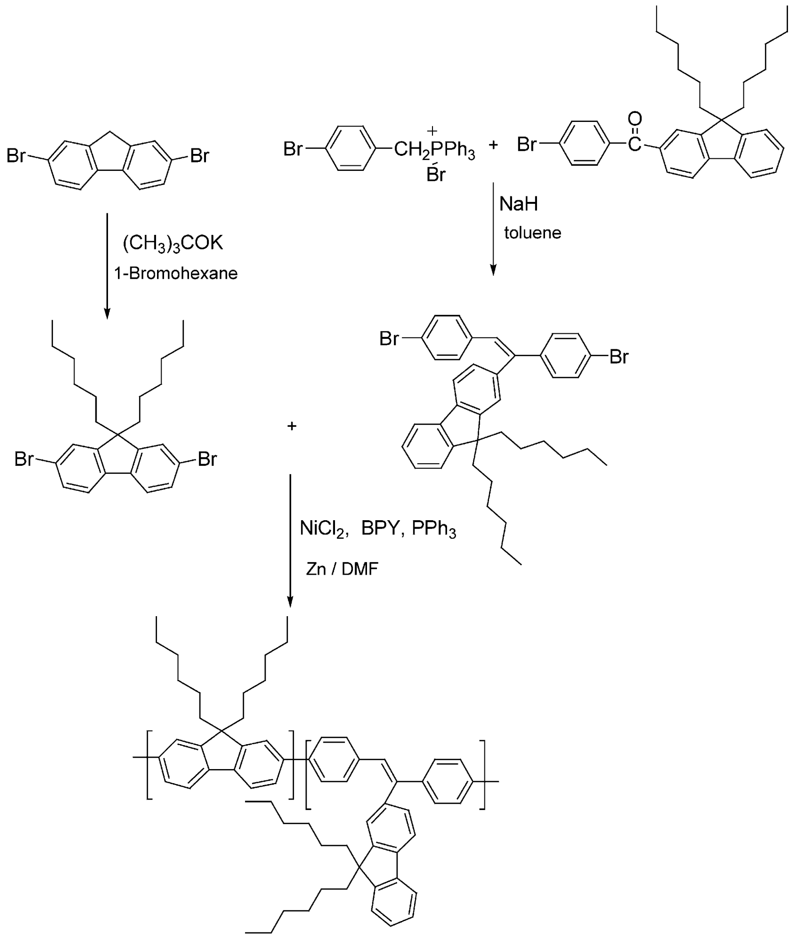
2. Experimental

All reagent and solvents were purchased from Aldrich Chemical and Co. and Fluka. Only analytical grade quality chemicals used. PEDOT was purchased from Bayer. Spectroscopies grade $CHCl_3$ (Aldrich) was used for all absorption and emission experiments. All other compounds were used as received.

1,2-Bis(4′-bromophenyl)-1-(9″,9″-dihexyl-3-fluorene) ethene (BPHFE) and 2,7-dibromo-9,9-dihexylfluorene were obtained by same method in literature [11,26].

2.1. Preparation of polymer

Into a 10 mL three necked flask equipped with a nitrogen



Scheme 1.

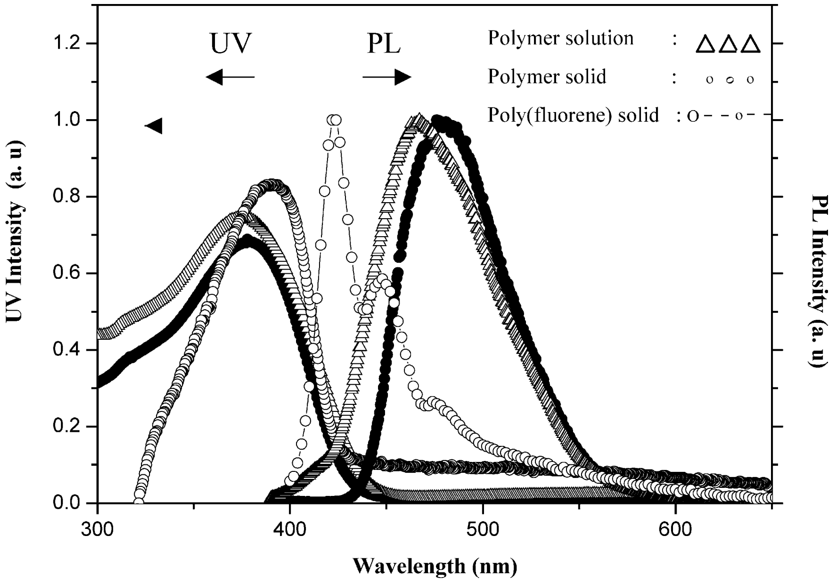


Fig. 1. UV–vis and photoluminescent spectra of polymer and poly(fluorene).

inlet, BPHFE (0.025 g, 0.375 mmol) and 2,7-dibromo-9,9-dihexylfluorene (0.1845 g, 0.375 mmol), nickel chloride (0.0095 mg, 0.75 mmol), zinc (0.2256 g, 1.125 mmol), bipyridine (0.117 g, 0.075 mmol), and *N*,*N*-dimethylformamide (DMF) (2.0 mL) were added under nitrogen. The reaction mixture was stirred at 90 °C for 12 h. After stirring, excess bromobenzene was added in the reaction mixture for end capping. After adding of bromobenzene, the reaction mixture was stirred at 90 °C for 6 h. The products were participated into a large excess of 20% hydrochloric acid/methanol solution. The white yellow solid that remained was washed with methanol, water, and methanol sequentially. The polymer was collected and dried under vacuum. The yield of the polymer after complete work up was 90 (%).

2.2. Fabrication of the LED

Poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) (PEDOT) for a conducting polymer hole injection layer (30–40 nm) was coated on an indium tin oxide coated glass substrate which had been washed with water, acetone, and isopropyl alcohole sequentially. A thin polymer film (80–110 nm) was spin coated (2200 rpm, 50 s) from a filtered (0.2 μm filter) 2.0 wt% of BPHFE solution in chlorobenzene on a PEDOT layer. LiF was vacuum-deposited as an electron injection layer (1–4 nm). An aluminium electrode (130 nm) was deposited on top of the device at a high vacuum (below 1×10^{-5} Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

3. Results and discussions

The synthesis of the monomer and the polymer is outlined in Scheme 1. 1,2-Bis(4′-bromophenyl)-1-(9″,9″-dihexyl-3-fluorenyl) ethene and 2,7-dibromo-9,9-dihexylfluorene were synthesized according to the procedures from the literature [26]. The random copolymerization with 1,2-bis(4′-bromophenyl)-1-(9″,9″-dihexyl-3-fluoreny) ethene as fluorenylstilbene unit and 2,7-dibromo-9,9-dihexylfluorene as fluorene unit was carried out using a nickel-catalyzed coupling reaction in good yield.

Molecular structure of the monomer and the corresponding EL polymer was identified by ^{1}H NMR and IR spectroscopy. In the IR spectra, the disappearance of the characteristic aromatic C–Br stretching in 1035/cm confirmed the polymerization. The copolymer was also confirmed by ^{1}H NMR with comparing the peak area at 7. 1 ppm of the vinyl proton peak and 2.0 ppm of a methylene in the hexyl group. The obtained polymer has good solubility in common organic solvents such as toluene, chloroform, methylene dichloride, and chlorobenzene. The number average molecular weight of the polymer, as determined by size-exclusion chromatography using polystyrene standards, was $M_n = 11{,}000$ (PDI = 1.64). Thermal behavior of the resulting polymer was investigated by DSC and TGA. The DSC measurement showed a glass transition at around 155 °C. The TGA thermogram of copolymer revealed that the copolymer has good thermal stability, showing a 5% weight loss at 430 °C under a nitrogen atmosphere.

Fig. 1 shows the optical absorption and photoluminescence spectra of polymer in solution and solid. The polymer in a chloroform solution exhibited absorption maximum at 380 nm due to the $\pi\rightarrow\pi^*$ transition of the conjugated polymer backbone with a shoulder at 315 nm which is a

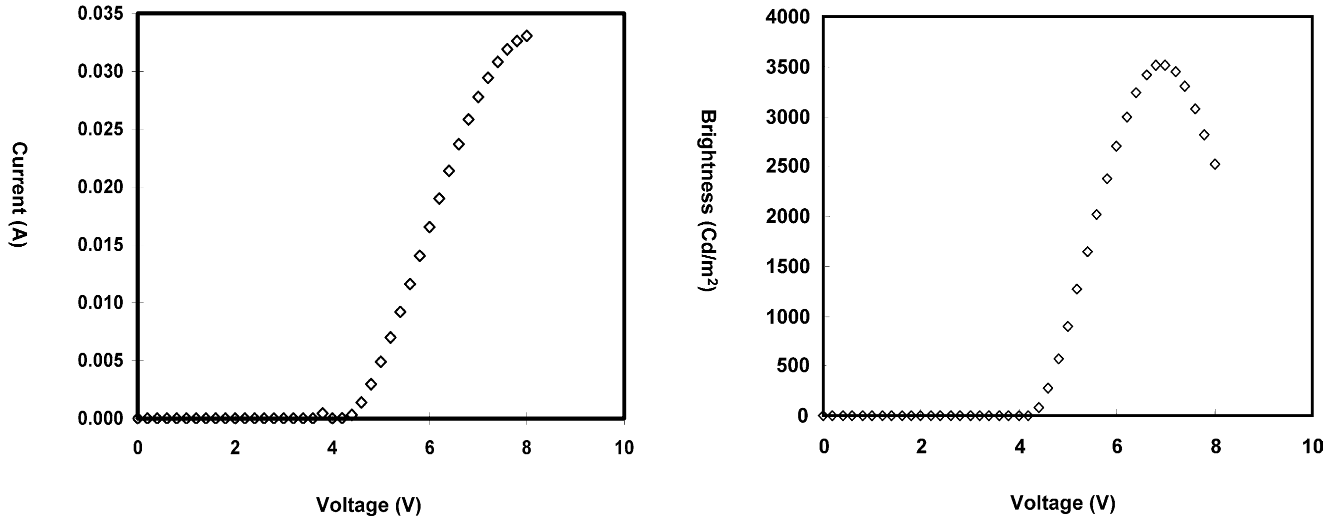


Fig. 2. Current–voltage and brightness–voltage characteristics of ITO/PEDOT/polymer/LiF/Al device.

characteristic peak of a fluorene unit in a solution. The absorption of thin film also shows a maximum in absorption at about 380 nm with the absorption edge at 448 nm. The maximum absorption peak of the polymer is 5 nm blue shifted compared with poly(fluorene), and 20 nm red shifted as compared with that of poly[4,4′-biphenylene-α-(9″,9″-dihexyl-3-fluorenyl)vinylene] which is homopolymer of BPHFE [26].

The polymer shows blue fluorescence in both solution and the solid state, though the maximum emission peak of the polymer is red shifted as compared with that of poly(fluorene). The PL spectrum of the dilute solution was almost consistent with that of film state. The result supposed that the aggregation and intermolecular interaction are completely suppressed by introduction of fluorenylstilbene with bulky fluorene pendant. Cyclic voltammetry was performed on a film of polymer deposited on a carbon electrode measured in AgNO$_3$ (0.01 M) /Bu$_4$NBF$_4$ (0.1 M)/acetonitrile with a platinium counter electrode and silver reference electrode, calibrated against ferrocene–ferrocenium. The oxidation peak potentials of poly(9,9-dihexylfluorene), poly[4,4′-biphenylene-α-(9″,9″-dihexyl-3-fluorenyl)vinylene] and the obtained random copolymer were measured to be and $E_{ox}=1.3$ V, $E_{ox}=1.15$ V and $E_{ox}=1.14$ V, respectively. From the result, it is supposed that the introduction of fluorenylstilbene comonomer lowered the oxidation potential to lead feasible hole injection. The reduction potential of random copolymer was $E_{red}=-1.78$ V. The optical energy band gap was 2.92 eV, and it was consistent with the result of the optical absorption threshold (448 nm).

The double layer PLED with the configuration of ITO/PEDOT/polymer/LiF/Al device was fabricated to investigate the EL property of polymer. Fig. 2 shows the current–voltage and brightness–voltage characteristics of device. The turn on voltage of device was approximately 4.4 V. The maximum brightness and the maximum efficiency of device was 3500 cd/m^2 and 0.878 lm/W, respectively. The power efficiency of device was increased when it is compared with that of fluorene homopolymer and BPHFE homopolymer [26,32,33]. The result may be due to balanced charge carriers resulted from easy hole injection and(or) inhibited intermolecular interaction and aggregation.

Fig. 3 shows the EL spectra of ITO/PEDOT/polymer/LiF/Al device at low voltage and high voltage. The electroluminescence spectra of polymer had maximum at about 468 nm without reference to voltage. The obtained EL spectra were almost identical to that of PL spectrum. The result suggests that the aggregation and intermolecular interaction are suppressed by randomly introduced fluorenylstilbene comonomer with bulky fluorene pendants. As a result of inhibited excimer, the emitting color of device was blue

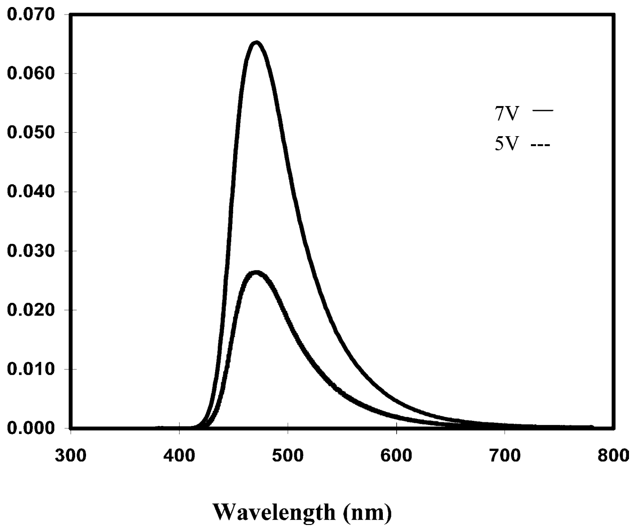


Fig. 3. The electroluminescent spectra of ITO/PEDOT/polymer/LiF/Al device at low voltage and high voltage.

$((x,y) = (0.17, 0.25))$ in CIE (Commission Internationale de l'Eclairage) chromaticity coordinates. The emission band with a full width at half maximum (FWHM) was 75 nm.

4. Conclusion

We synthesized a random copolymer having fluorene and fluorenylstilbene by Yamamoto coupling. The random copolymer had the low oxidation potential, compared with poly(fluorene). The polymer in thin film emits strong blue luminance with narrow bandwidth upon photoexcitation. PL spectrum of the polymer in the film is almost consistent with that of solution one as well as the EL spectrum, indicating that the aggregation and the excimer fluorescence are suppressed. The ITO/PEDOT/polymer/LiF/Al device showed the maximum brightness of 3500 cd/m^2, the maximum efficiency of 0.878 lm/W and blue emission with CIE chromaticity coordinates of $((x,y) = (0.17, 0.25))$. The randomly introduced fluorenylstilbene comonomer tunes the HOMO level of polymer as well as suppresses the excimer formation due to intermolecular interaction. Thus, it leads to keep stable blue color and to have high efficiency.

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