

Color Tuning of PLED based on Poly(fluorene)s

Jeong-Ik Lee, Lee-Mi Do, Hye Yong Chu, Sung Hyun Kim, and Taehyoung Zyung

Abstract

To obtain various colors from the blue emitting poly(fluorene)s, two different approaches are introduced. One is copolymerization with low band gap comonomers and the other is molecular doping with various dyes. As fast and efficient exciton migration and trapping and/or energy transfer between the chromophoric segments or doped dyes in conjugated polymers can shift the emission to longer wavelengths, these phenomena can be utilized to obtain various colors from the intrinsically blue light emitting poly(fluorene)s.

Keywords : light emitting diodes (LED), polymer, poly(fluorene), and color tuning

1. Introduction

Conjugated polymers have attracted much attention as a promising in the past several decades as an electroactive materials in various applications including batteries, molecular electronic devices, light emitting diodes (LEDs), etc [1]. Especially, electroluminescence has attracted much interest as a promising application in polymeric LEDs of semiconducting polymers [2]. Poly(fluorene)s are good materials for light emitting diodes because of their high photoluminescence (PL) quantum efficiencies and thermal stability [3-5]. The fluorene structural unit provides rigidly planarized biphenyl units within the polymer backbone and the possibility of remote functionalization at C-9, hence improving both polymer processability and mediating potential interchain inter-actions in films.

There are two different methods for obtaining various colors from the LEDs based on poly(fluorene)s. One is copolymerization with low band gap comonomers. As fast and efficient exciton migration and trapping between the chromophoric segments in conjugated polymers can shift the emission to longer wavelengths, we can exploit this phenomenon can be utilized to obtain various colors from the copolymers based on the intrinsically blue light

emitting poly (fluorene)s [4, 6]. The other method is molecular doping with various dyes which can convert the blue emission of poly(fluorene) into the emissions of doped dyes. To transfer the energy of poly(fluorene) exciton to doped dyes, the homo and the lumo of doped dyes must be located between the HOMO and the LUMO of poly (fluorene). Therefore, careful consideration should be taken in choosing the doping dyes.

In this paper, we demonstrate color tuning in poly (fluorene) derivatives by molecular doping with various dyes and incorporating low band gap comonomers in the poly(fluorene) main chain.

2. Experimental

4,4'-Dibromo- α -cyanostilbene (CNSt), 1,4-bis(2-(4'-bromophenyl)-1-cyanovinyl)-2-(2'-ethylhexyl)-5-methoxybenzene (BCNVB) and an inseparable mixture of 3,9- and 3,10-dibromoperylene (PER) were used as the low band gap comonomers. Various high molecular weights, readily soluble homopolymers and copolymers derived from 2,7-dibromo-9,9-bis(2'-ethylhexyl)fluorene (BEHF) and the low band gap comonomers were prepared using zero valent nickel (Fig. 1) [4]. Coumarin 6, and PtOEP were purchased from Aldrich chemical company and Porphyrin, respectively. The synthesis of BDMOSPPV has already been reported in the previous paper [7]. Thin films of polymers were obtained by spincoating from polymer solutions in cyclohexanone on fused quartz plates. All the

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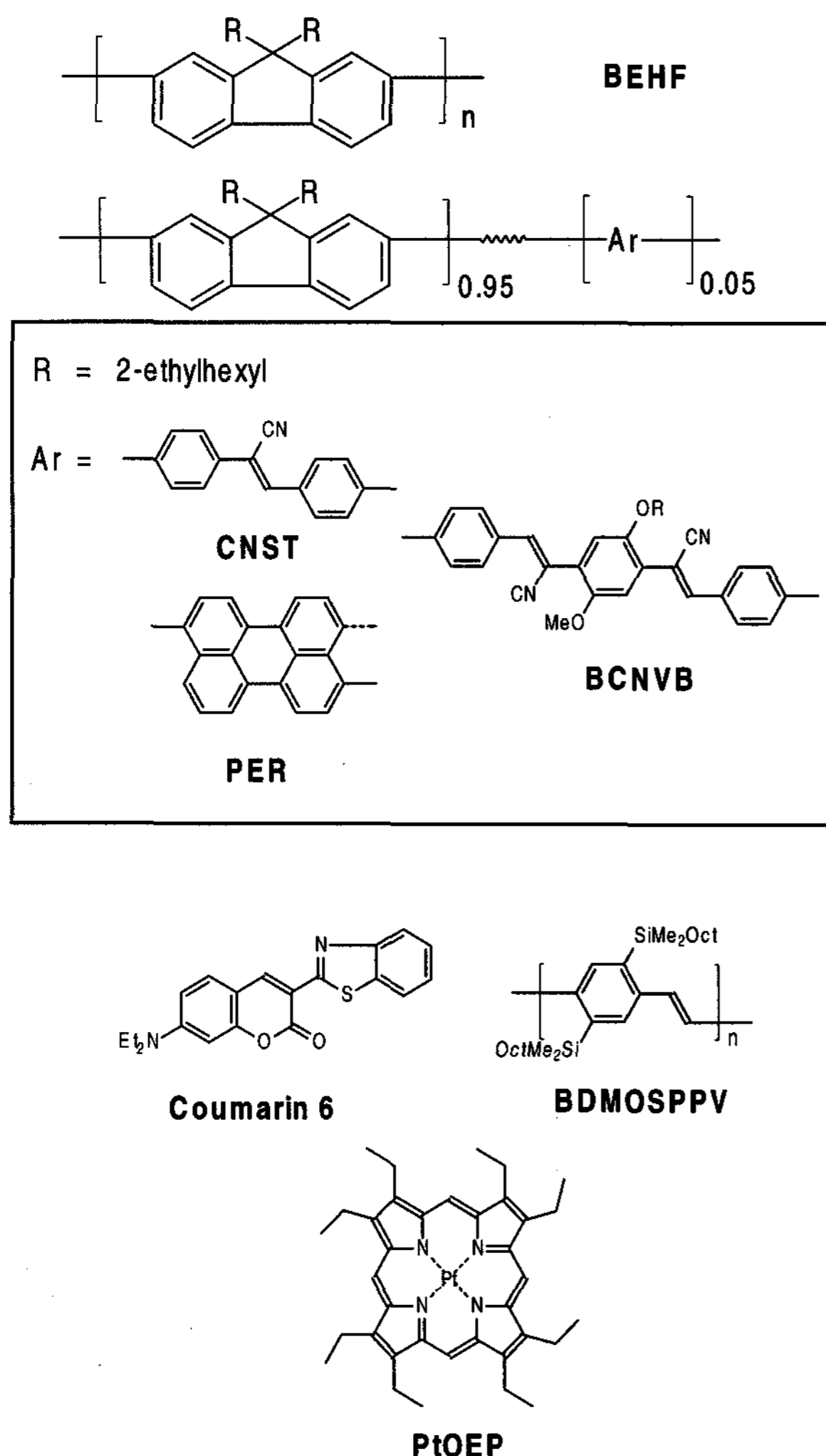


Fig. 1. Chemical structures of the polymers, the comonomers and the doping dyes.

photo-physical measurements were performed at room temperature. The absorption spectra were measured by using a Hewlett Packard diode array spectrophotometer model 8452A. Steady-state photoluminescence spectra were recorded on a Spex FL3-11.

Single layered LEDs utilized the homopolymers and copolymers as an emitting layer in single-layered LEDs with ITO anodes and Aluminum (Al) cathodes. The polymer layer was spin-coated to a thickness of ~ 100 nm. A patterned Al cathode (100 nm) was then deposited by thermal evaporation. Electroluminescence (EL) spectra were recorded using Minolta CS-1000 and Current-voltage (I-V) and radiance-voltage characteristics of the devices were simultaneously measured with a Keithley 2400 Source Measure Unit and a Minolta LS-100.

3. Results and Discussion

The concept of exciton migration and trapping offers intriguing possibilities for color tuning in poly (fluorene) derivatives. The branched 2-ethylhexyl substituents were employed to improve the solubility of the resulting copolymers.

The spectroscopic properties of the low band gap comonomers before polymerization were measured in THF solution. From the absorption spectra of the comonomers, we could qualitatively estimate the band gap of the comonomers (not shown here). As the absorption maxima/band edges of comonomers in THF solution were 360/410 for CNSt, 374/430 for BCNVB and 440/450 nm for PER, the PER and CNSt had the lowest and the highest band gap, respectively, while that of BCNVB is intermediate. The mole % of comonomers in each of the examples was 5%. In the copolymer films, there was no short wavelength PL emission, which is a characteristic of fluorene units (Fig. 2). The PL spectra showed only the long wavelength emission from the chromophoric units containing the corresponding low band gap comonomers, while the blue emission band from fluorenyl units was observed in the THF solutions. These results were rationalized by the possibility of efficient exciton migration to chromophoric trapping sites. The excitons produced by direct excitation apparently migrated to lower energy trapping sites containing the low band gap comonomers, which then emitted light. This phenomenon is particularly efficient in films, but much less so in solution, hence suggesting the importance of interchain communication in solid films.

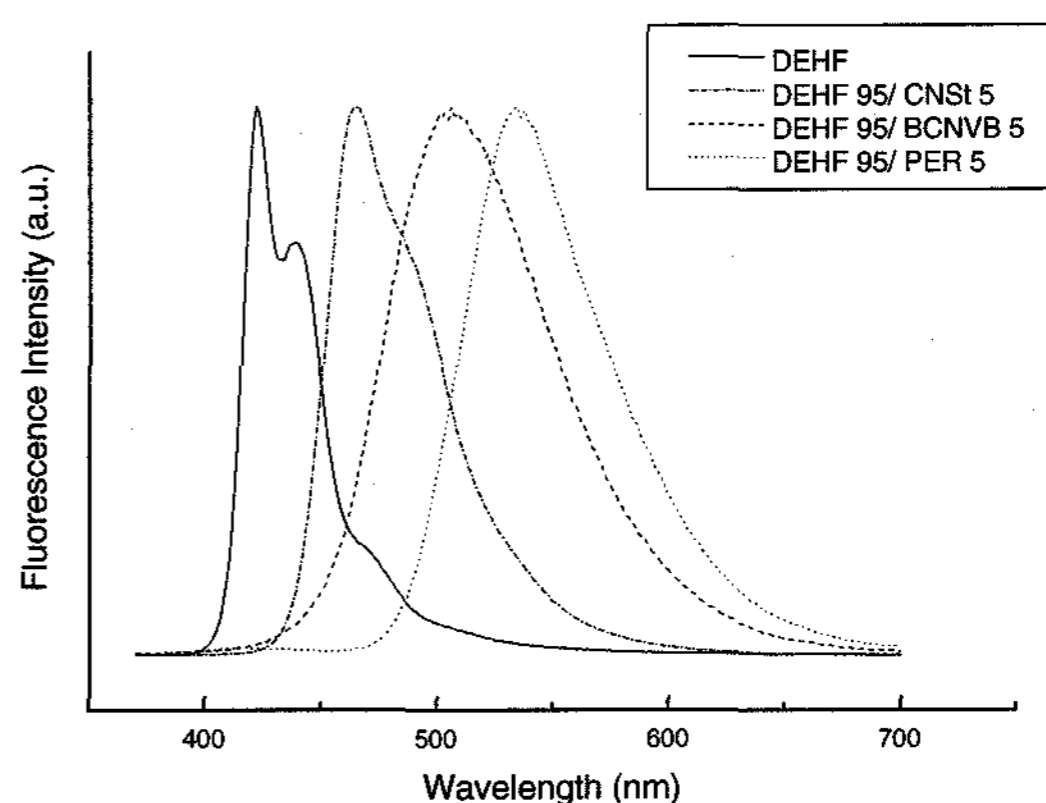


Fig. 2. Photoluminescence spectra of poly(fluorene) copolymers. Excitation wavelength was 380 nm.

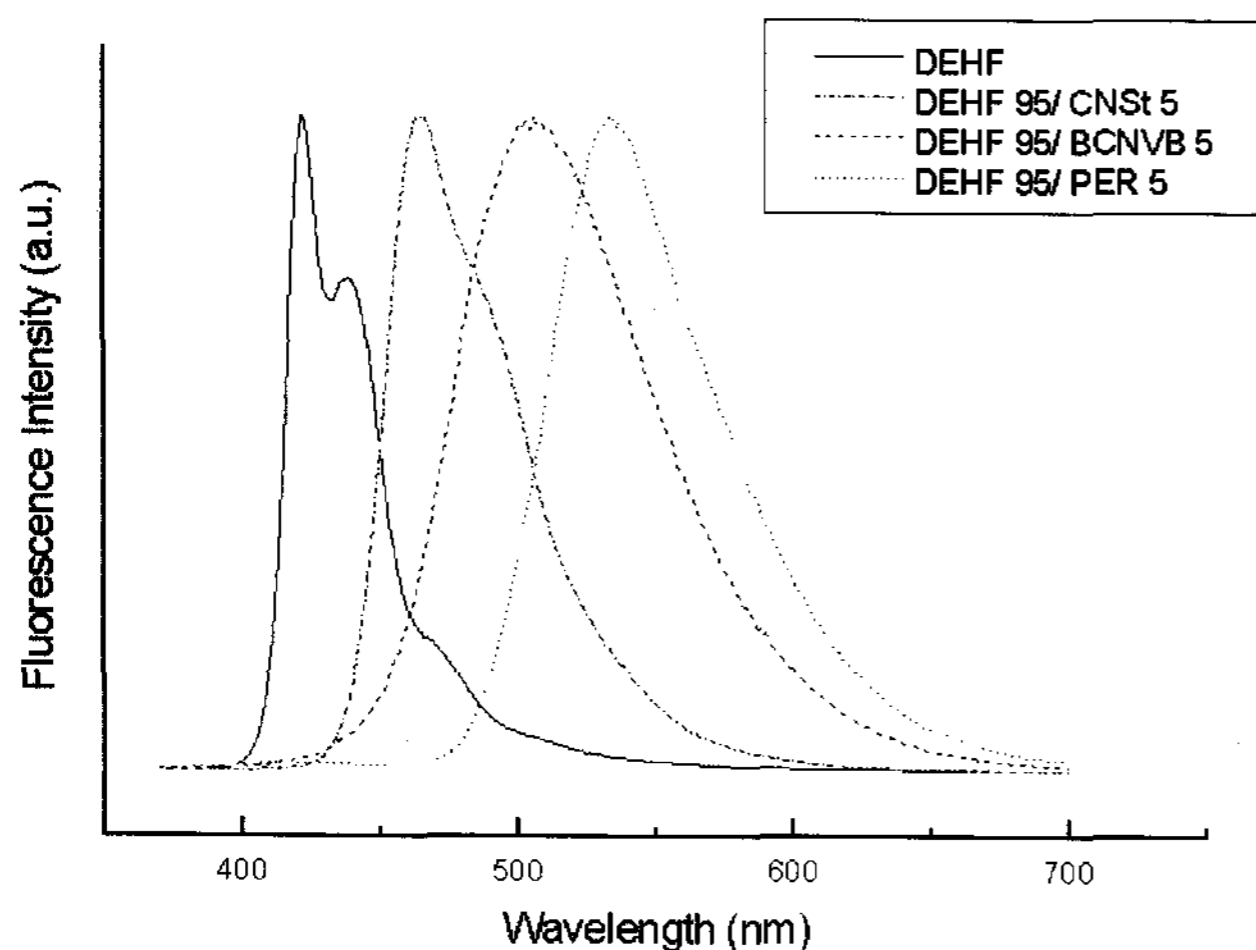


Fig. 3. Electroluminescence spectra of poly(fluorene) copolymers; device configuration ITO/polymer/Al.

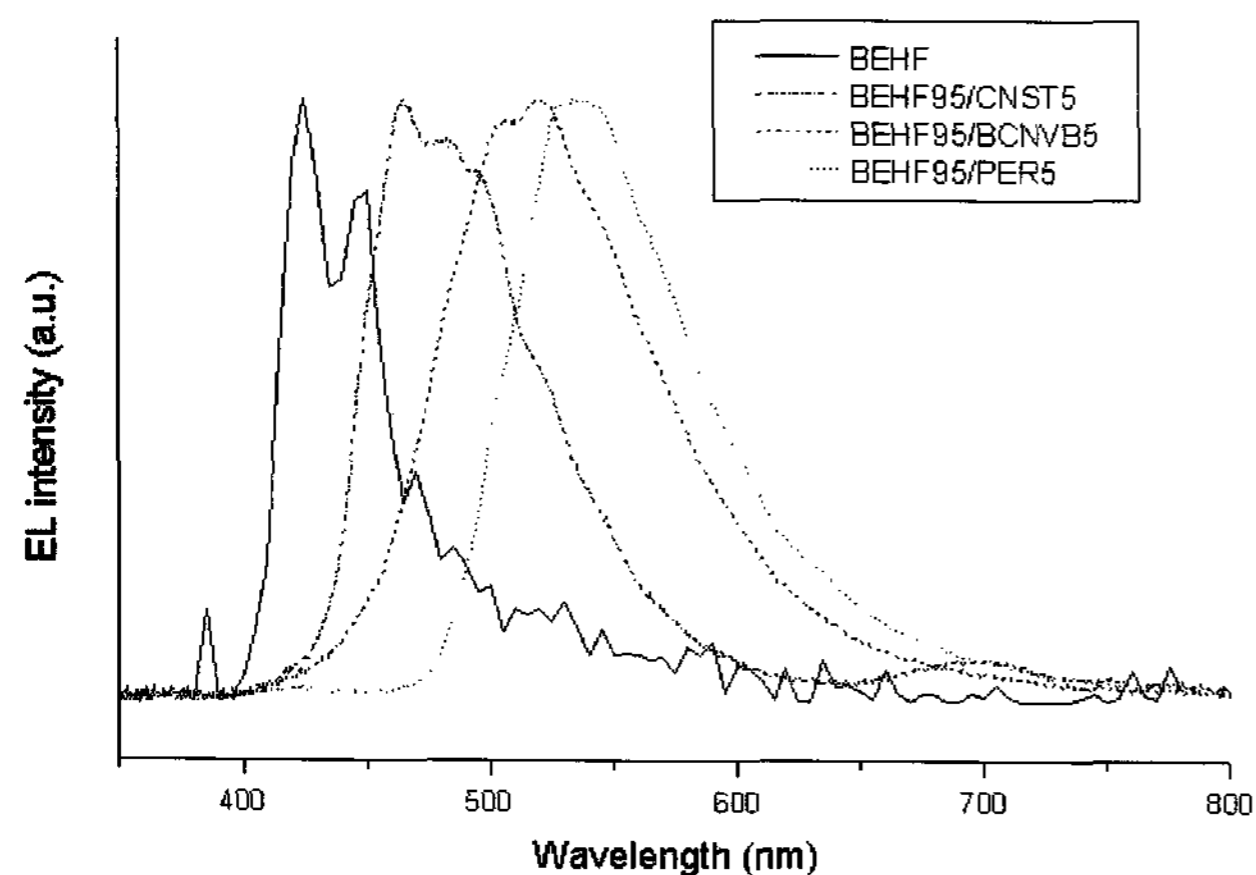


Fig. 4. Photoluminescence spectra of poly(fluorene) doped with various dyes. Excitation wavelength was 380 nm.

Fig. 3 shows the electroluminescence (EL) spectra of the copolymers are shown in comparison with that of the BEHF homopolymer. As expected from the absorption edges of comonomers or band gap of comonomers, the sequence of electroluminescence maxima when they are incorporated in poly(fluorene) is as follows; CNST < BCNVB < PER. Thus, we can easily vary the emission colors by incorporating only very small amounts of comonomers with lower band gaps into the intrinsically blue light emitting poly(fluorene) homopolymers. We are in the process of finding appropriate comonomers which can be polymerized with fluorene and changed to right green and red emitting polymers.

The other method for tuning color by using poly

(fluorene) is molecular doping with various dyes. Polymeric materials as well as low molecular weight dyes can be used as doping materials, which can be also be used in small molecule organic light emitting diode as dopants [8, 9]. In this study, Coumarin 6 and poly(2, 5-bis (dimethyloctylsilyl)-1, 4-phenylene vinylene) (BDMOSPPV) for green emission and platinum(II) octaethylphosphyrin (PtOEP) for red were used. PtOEP is the most promising candidate for red color display to date. It shows exceptionally high efficiency due to triplet emission [10]. BEHF was employed as a host material and 5 wt% of dye doped polymer solutions were prepared. Relatively higher energy transfer has observed for Courmarin 6 doped polymer film, compared with other polymer films even though blue emission of poly(fluorene) has been remained a little (Fig. 4). For BDMOSPPV and PtOEP, however, 5 wt% was not enough to transfer blue emission of poly(fluorene) to the emissions of BDMOSPPV and PtOEP. Therefore, 25 wt% of polymer blend was prepared instead of 5 wt%.

Fig. 5 shows electroluminescence spectra of dye doped polymer devices. Despite the fact that Coumarin 6 is known as a green emitting dye, Coumarin 6 doped BEHF polymer device exhibits a bluish green colour due to non-polar polymer matrix. As for coumarin 6 doped polymer device, emission mostly from the dye was observed, like in PL. As shown in Fig. 6, the LUMO of coumarin 6 is lower

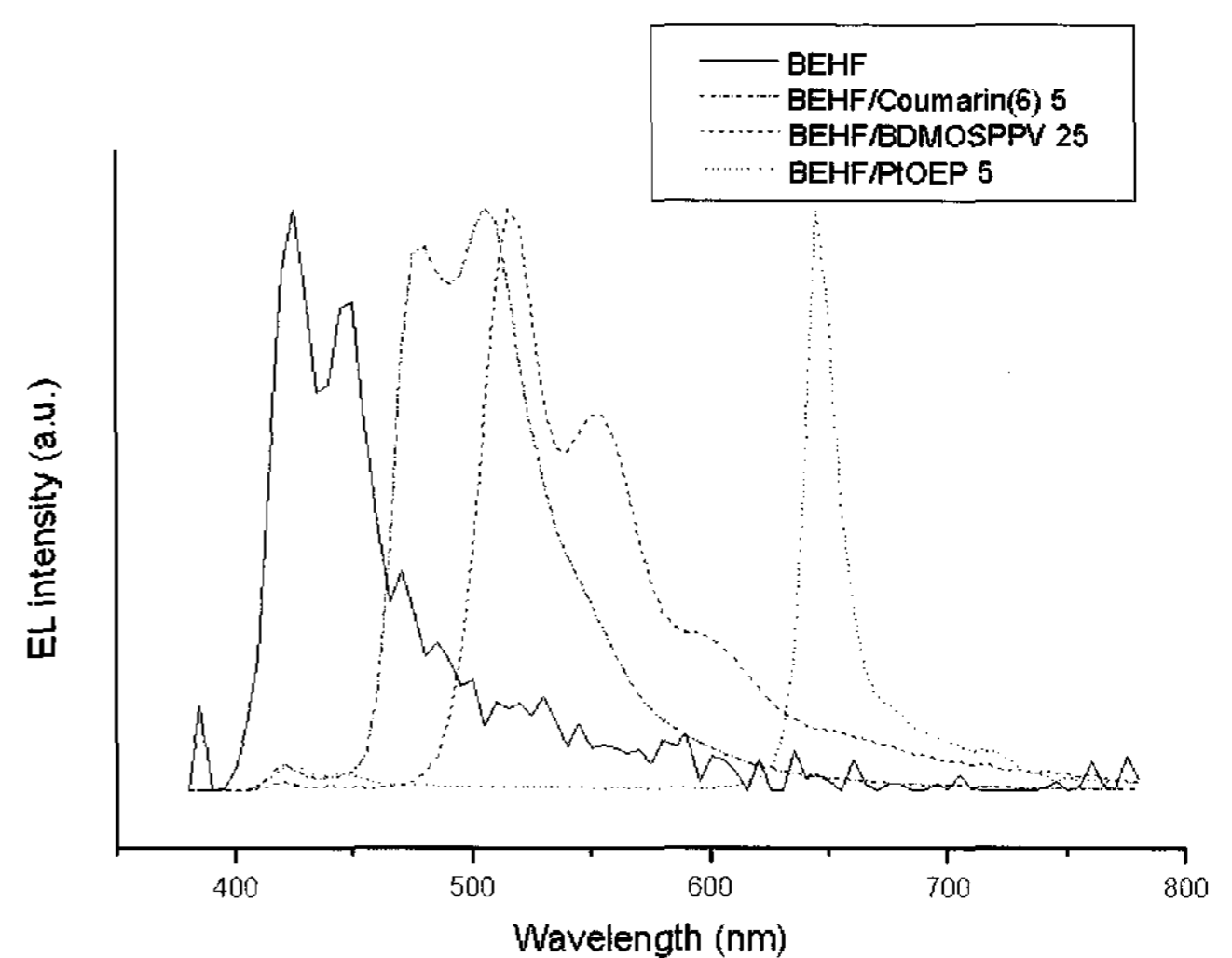


Fig. 5. Electroluminescence spectra of poly(fluorene) doped with various dyes; device configuration ITO/polymer/Al.

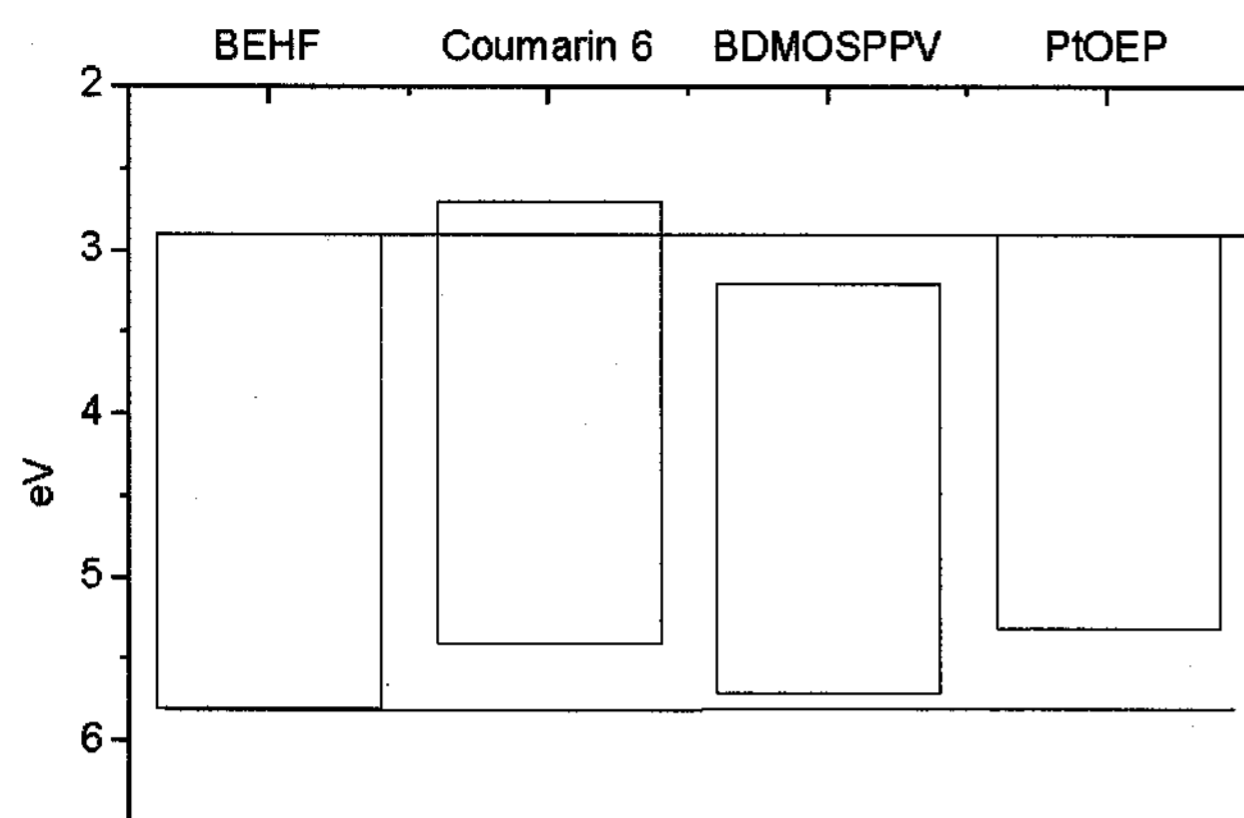


Fig. 6. HOMO and LUMO levels for the BEHF and dyes used in this study.

than the LUMO of BEHF while the HOMO is lower than that of BEHF [11] and therefore, the dominant coumarin 6 emission spectrum in this device can be explained by either charge(hole) trapping at coumarin 6 or exciton energy transfer from BEHF to coumarin 6. BDMOSPPV and PtOEP doped polymer devices showed green and red emissions, respectively. 25 wt% of BDMOSPPV was enough to convert blue emission into green emission while 5 wt% of BDMOSPPV was not enough [12]. Considering that the BDMOSPPV HOMO and LUMO are located between BEHF HOMO and LUMO, we initially assumed good energy transfer between them in both photoluminescence and electroluminescence. However, the results showed to be the opposite. This inefficient energy transfer could be explained by the phase separation which is yet to be investigated. As for PtOEP, 5 wt% was enough to obtain red emission although partial energy transfer was observed in photoluminescence spectrum. Recently, V. Cleave et al. reported about the transfer process in poly(fluorene) and PtOEP [13]. They explained that the transfer process between them in EL is charge recombination at guest and the PtOEP acts as a deep trap for hole due to the fact that the position of PtOEP HOMO is much lower than that of BEHF, hence causing energy transfer does not occur in this blend but hole trapping.

4. Conclusion

In this study, we were able to effectively tune the emission color in thin films by incorporating small amounts of the low band gap comonomers and molecular doping with the dyes. The efficient excitonic energy transfer and charge trapping played an important role in tuning electroluminescence colors in polymer light emitting diodes based on poly(fluorene)s. The device optimizations are still under investigation and the device characteristics will be reported after the device optimizations. Finding appropriate comonomers and doping dyes were also carried out to obtain the right green and red for display application.

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