Poly(fluorene)s for LED Applications

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Abstract

The emission color stability of poly(fluorene) derivatives upon thermal annealing or passage of current in an electroluminescent device is affected by the structure of the main chain polymer unit and particularly by the polymer chain end substituents. Proper attention to these features leads to colorfast blue emission in both photo- and electoluminescence. Furthermore, the spectral emission characteristics can be tuned by the incorporation of various comonomers. Preliminary single layer device studies validate the potential utility of poly(fluorene) homo and copolymers for OLED applications.

Introduction

Small molecules, oligomers and polymeric materials constitute the active components of organic light emitting diodes.[1,2] Some potential advantages of polymers over small molecules include higher glass transition temperatures, excellent film forming properties and simplified processing by spin coating. Many of the polymeric materials studied have been conjugated polymers. Within this class, poly(fluorene) derivatives are particularly interesting because of their thermal and oxidative stability, good processibility and their high emission quantum yields, even in the solid state.[2,3] A wide variety of substituted poly(fluorene) homo and random copolymers can be prepared by the nickel-mediated polymerization of various 2,7-dihalofluorenes and dihaloarylene comonomers.[4,5] Polymer molecular weights and end groups can be controlled by the addition of monofunctional derivatives at various points in the polymerization process. One potential problem with poly(fluorene) derivatives for OLED applications is the appearance of long wavelength emission bands upon thermal annealing or the passage of current in a device.[4,5] The latter is often manifested by the poor color stability during operation. One reason for this is the appearance of a long wavelength emission band which is attributed to excimer formation caused by morphology changes in the films. This long wavelength emission is exacerbated in electroluminescence spectra relative to photoluminescence. The appearance of this long wavelength emission depends on film morphology, molecular weight, end groups and polymer chain structure.[4,5] In this paper, we discuss these effects as well as the use of lower band gap comnomers to suppress excimer formation and tune the emission wavelength.

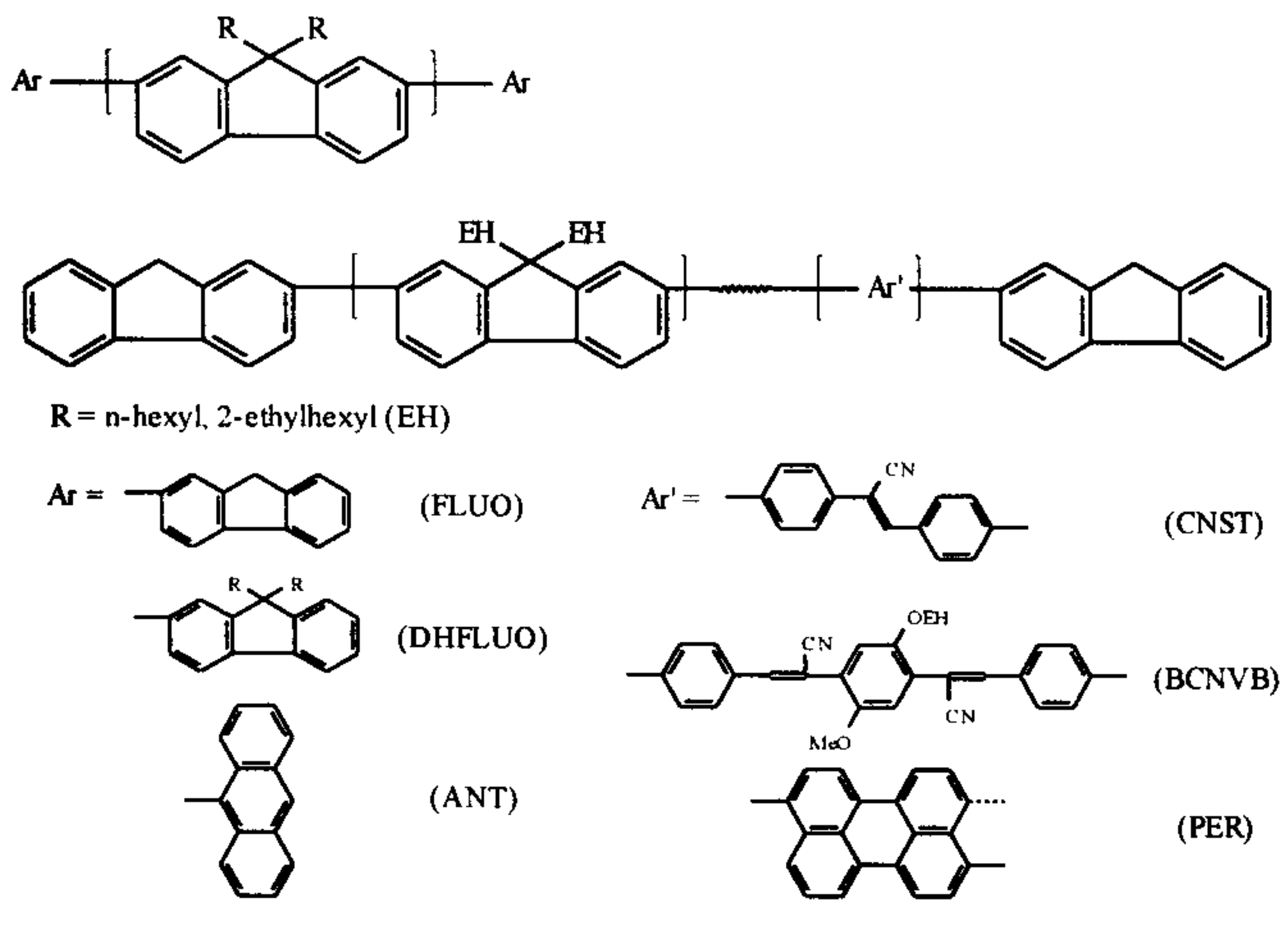

Fig. 1. Polymer structures.

Results and Discussion

A variety of end capped poly(fluorene) homo and copolymers were prepared by the nickel-mediated arylene polymerization shown in Figure 1. All of the polymers were soluble in common organic solvents and were characterized by ^{1}H-NMR, ^{13}C-NMR, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and gel permeation chromatography (GPC) using polystyrene as calibration standards. For the copolymer, the incorporation level of comonomer in the copolymers tracked the monomer feed ratio. The polymer properties of the homo and copolymer are reported in Table 1. In this table, the designation DHF-FLUO, DHF-DHFLUO, and DHF-ANT refer to the poly(di-*n*-hexylfluorene) homopolymer end capped with 2-bromofluorene, 2-bromo-9,9-di-*n*-hexylfluorene, and 9-bromoanthracene, respectively. With the true random copolymers, the monomer unit designators are separated with a slash (/). BEHF refers to 2,7-dibromo-9,9-bis(2'-ethylhexyl)-fluorene and the structures of CNST, BCNVB, and PER are shown in Figure 1.

We found that the nature of the chain end groups play a major, perhaps seminal role in the formation of the long wavelength emission upon thermal annealing under a nitrogen atmosphere. This is shown in Figure 2 which displays the emission spectra of DHF end capped with 2-fluorenyl, 9,9-di-*n*-hexyl-2-fluorenyl and 9-anthryl substituents after thermal annealing. It is clear that the relatively sterically unencumbered 2-fluorenyl substituent results in the largest amount of long wavelength

Table 1. Properties of poly(fluorene) homo and copolymers

Polymers	M_n (X 10^3)	T_g (°C)	λ_{max} (nm) absorption	λ_{ma}x (nm) emission
DHF-FLUO	15	97	380	423
DHF-DHFLUO	13	96	381	426
DHF-ANT	14	115	380	425
BEHF-FLUO	20	76	384	423
BEHF95/CNST5-FLUO	38	85	376	466
BEHF95/BCNVB5-FLUO	20	85	390	506
BEHF95/PER5-FLUO	40	85	378, 470	554

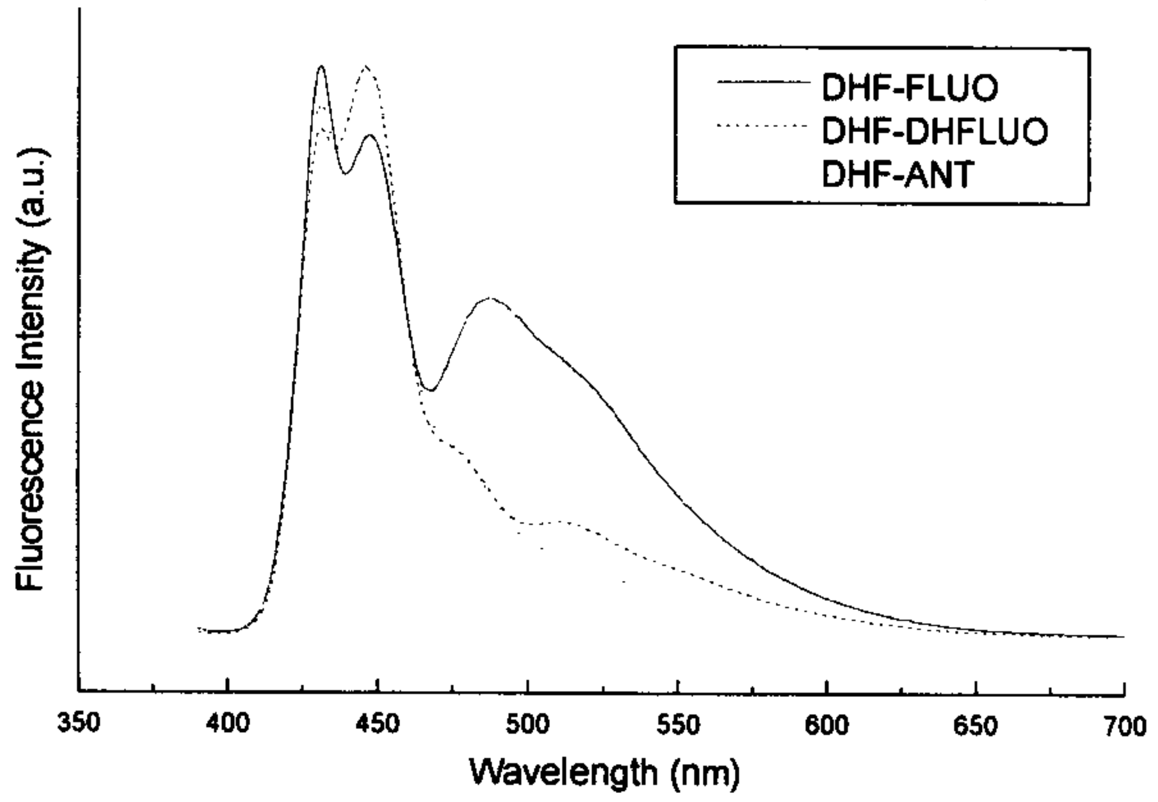

Fig. 2. Emission spectra of poly(fluorene)s with different end groups.

emission upon annealing. Adding di-*n*-hexyl substituents to the fluorene end groups significantly improves the situation, but some spurious long wavelength emission is still observed upon annealing. Surprisingly, the incorporation of 9-anthryl end groups into the DHF polymer completely suppresses the formation of long wavelength emission. It is remarkable that the presence of 9-anthryl end groups alone result in a colorfast emitting material validating the critical importance of the polymer chain ends in mediating the morphological changes resulting in the long wavelength emission.

The concept of exciton migration and trapping provides intriguing possibility for color tuning in poly(fluorene) derivatives.[6] It also provides a route to mitigating the formation of poly(fluroene) excimers providing the concentration of the low band gap comonomers in the copolymers is low and excitonic energy transfer to the low energy segments is rapid. The electronic and polymer properties of the copolymers are described in Table 1. The mole % of comonomers in each of the examples was 5%. Figure 3 (a) shows the film emission spectra of BEHF homopolymer and the respective 95/5 copolymers. In the case of the copolymers, the intrinsic blue emission of the poly(fluorene) fragments is completely suppressed and is replaced by a red shifted emission band characteristic of the lower band gap comonomer segments. The emission wavelengths progressively red shift as the comonomer is varied from CNST to BCNVB to perylene. The spectral emission of poly(fluorene) copolymers can be spectrally tuned by the addition of small quantities of comonomers with appropriate electronic characteristics. For these samples, thermal annealing of the films causes almost no change in the respective emission spectra. In this regard, the behavior of the copolymers is distinctly different from that of the BEHF homopolymer where thermal annealing results in the appearance of a broad red shifted emission caused by the formation of excimer.

As discussed earlier, the appearance of excimer emission in poly(fluorene) derivatives is often exacerbated in electroluminescence relative to photoluminescence. The electroluminescence spectra of the copolymers are shown in Figure 3 (b) in comparison with that of the BEHF homopolymer. In the case of the copolymers, the EL and PL spectra are very similar while the EL spectrum of the BEHF homopolymer shows relatively more red shifted emission than in the PL spectrum of the annealed material. Likewise, the EL spectrum of the end capped materials DHF-ANT (not shown here) is very similar to its respective PL spectrum before and after thermal annealing. From this, we conclude that end capping with appropriate reagents can lead to color fast emission in poly(fluorene) derivatives even in electroluminescence devices.

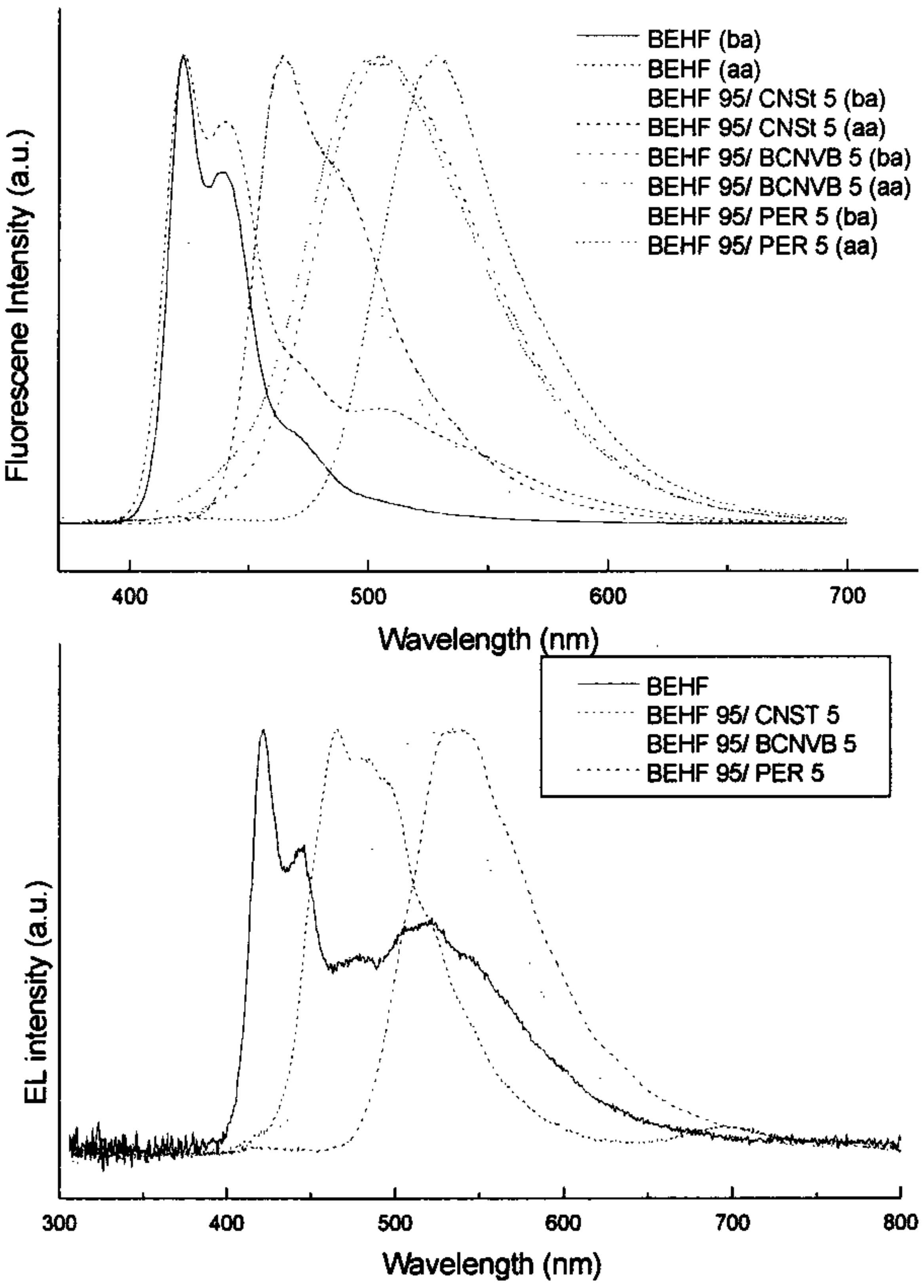

Fig. 3. (a) Solid state emission spectra of poly(fluorene) copolymers; ba and aa stand for before and after thermal annealing at 200 °C for 4 hours in nitrogen. (b) Electoluminescence spectra of poly(fluorene) copolymers; device configuration ITO/polymer/Ca.

In summary, we have found that the emission color stability of poly(fluorene) homopolymers is affected by the structure of the main chain units and the nature of the end capping subsitutents. Proper attention to these features leads to colorfast blue emission in both photo- and electoluminescence. Furthermore, the spectral emission characteristics can be tuned over a wide range by the incorporation of small amounts of appropriate comonomers. Preliminary single layer device studies validate the potential utility of poly(fluorene) homo and copolymers for OLED applications.

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