New red light-emitting copolymer based on polyfluorene

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Abstract

We report a new red light emitting fluorene-based copolymer, poly{9,9-bis(2'-ethylhexyl)fluorene-2,7-diyl-co-2,5-bis(2-thienyl-1-cyanovinyl)-1-(2'-ethylhexyloxy)-4-methoxybenzene-5'',5'''-diyl} (PFTCVB). The synthesized copolymers showed the absorption maxima at about 380 nm and the absorption between 425 and 600 nm increased as the fraction of the thiophene-containing monomer (BTCVB) increased. In PL, the emission maxima of the copolymers were red-shifted as the fraction of BTCVB increased, despite the similar absorption characteristics were shown in the UV-visible spectra. The copolymer containing 15 mol% of BTCVB showed a maximum PL and EL emission at 620 and 630 nm.

1. Introduction

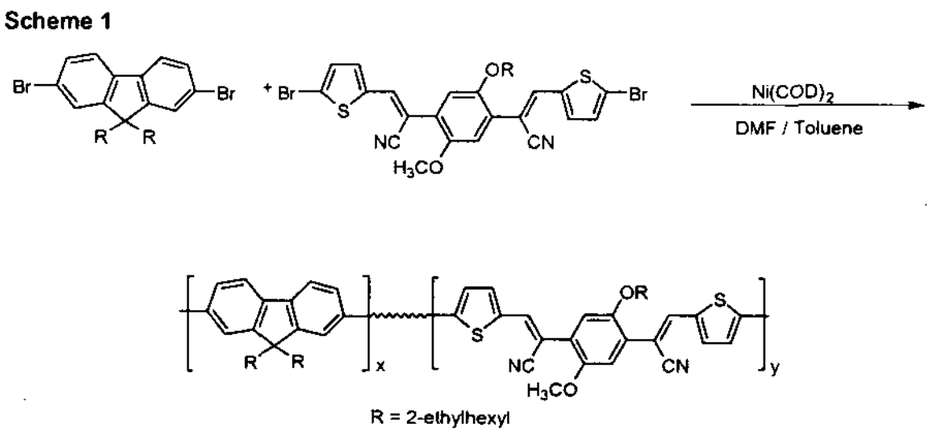
Since the initial report of polymeric light-emitting diodes based on PPV by the Cambridge group[1], enormous effort has been devoted to the synthesis of light emitting polymers because of their potential applications as active materials for organic electroluminescent displays.[2-4] The simple structure of a polymeric light-emitting diode consists of a anode with a high work function such as indium tin oxide (ITO), a cathode with a low work function such as Al, Mg, or Ca, and the light-emitting polymer sandwiched between these two electrodes. In this device structure, the holes and electrons are injected through each anode and cathode. And then, the injected holes and electrons migrate across the polymeric layer and combine to form excitons, which then decay with photon emission. Therefore, many efforts have been to optimize efficient and balanced charge injection, good mobilities for both holes and electrons, and high efficiency. Moreover, there have been many reports in chemical structures in polymers - depending on chemical structure of the emissive polymer, different colors can be obtained.

In this regard, there are many conjugated polymers reported in order to obtain the three primary colors, for examples, poly(*p*-phenylene)s, poly(oxadiazole)s, poly(fluorene)s, and so forth. Among these polymers, polyfluorene derivatives have shown to emit colors spanning the whole

visible range with high efficiency and low operating voltage. Recently, we reported the poly(fluorene) based red light-emitting polymer made from random copolymerization using energy transfer.

Along these lines, we report here new red light-emitting polyfluorene derivatives, PFTCVBs. The synthetic routes and details are given in Scheme **1.**

Scheme 1



2. Result

2.1 Optical Properties.

Figure **1** shows the UV-vis absorption spectra of the thin films of PFTCVBs coated onto fused quartz plates. All of the PFTCVBs exhibit absorption maxima close to 380 nm, regardless of copolymer composition. The absorption maxmum of PFTCVB15 is slightly blue-shifted because of its high molecular weight contrary to the copolymer having low molecular weight. As the fraction of BTCVB increases, however, the absorption between 425 and 600 nm increases. These absorption bands could be due to the BTCVB units incorporated into the polyfluorene main chain, and the increase of this unit affects the absorption intensities because of the low band gap of BTCVB. The film of PBEHF homopolymer showed PL emission maxima at 420 nm and 440 nm. Interestingly, these two strong and sharp PL peaks reduce in size dramatically in the PL spectra of the PFTCVBs, as shown in Figure **2**. In contrast, the emission peaks from the BTCVB part increase greatly, such that even PFTCVB1 (which contains only 1.4 mol% of BTCVB) clearly exhibits this phenomenon. PFTCVB1 greatly shifted its PL maximum to 540 nm with a large and broad shoulder at 575 nm. These large shifts in PL maxima are probably due to intramolecular energy transfer from the BEHF part to BTCVB chromophores. Therefore, the emission from the latter is major in PL spectrum. The emission maxima of the copolymers gradually shift to the long wavelength as BTCVB content increases. This shift in the emission maxima might be explained that the number of BTCVB unit in copolymer increases when the fraction of BTCVB in polymerization increases. As a result, PFTCVB15 showed a PL emission maximum at 620 nm, yielding red emission. Conclusively, we succeeded in embodying full colors from blue to red with these new fluorene-based copolymers by making small changes in the amount of red-emissive BTCVB.

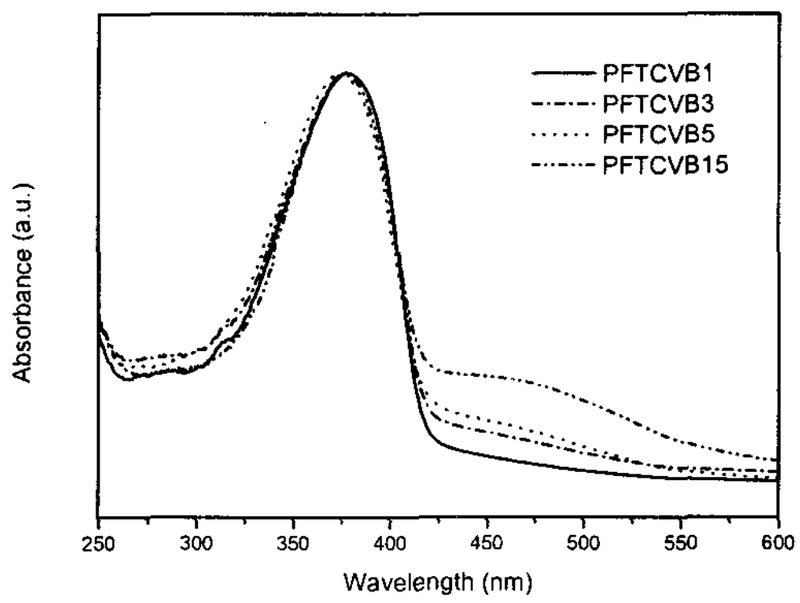


Figure 1 UV-visible spectra

In Figure 3, EL spectra are shown with device structure of ITO/PEDOT/polymer/LiF/Al. EL spectra of the PFTCVBs are similar to the PL spectra of the copolymers with the same components (Figure **3**), which indicates that the same energy transfer is involved in EL and PL. It is reasonable to suppose that these results are due to energy transfer from the high-energy-state fluorene moiety to the low-energy-state BTCVB moiety. As a result, the transferred excitons decay through radiative recombination in BTCVB and then exhibit a red-shifted emission in comparison to the emission of the homopolymer. In particular, PFTCVB15 (which contains 17.5 mol% of BTCVB) showed almost pure red emission at 630 nm.

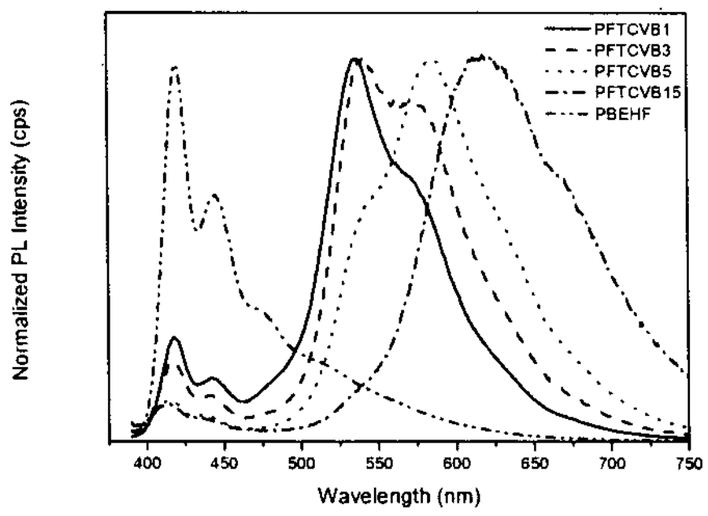


Figure 2 Photoluminescence Spectra

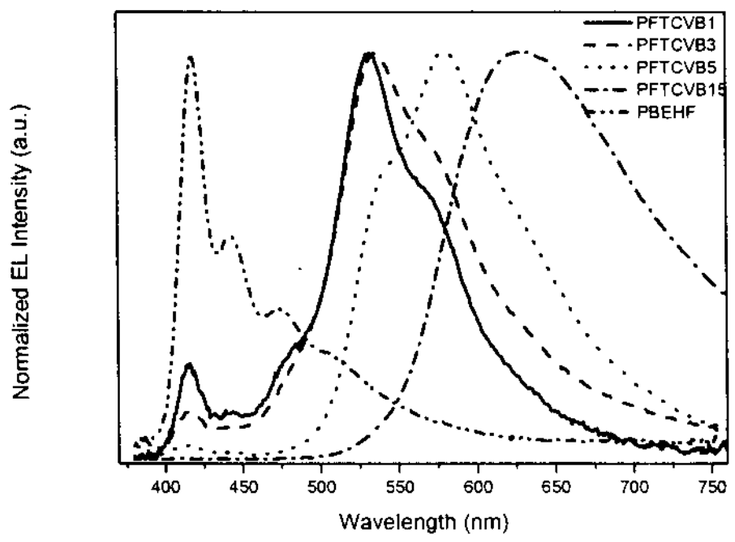


Figure 3 Electroluminescence Spectra

3. Summary

Polymeric light emitting diodes(PLED) are promising a new display technology because of lots of advantages for flat panel displays such as low turn-on voltage, relatively high quantum efficiency, easy processibility, good mechanical strength, and color tunability. As a result, PLED are now considered as a very important class of LED materials by both academic and industrial laboratories.

PFTCVBs are a new fluorene-based red light emitting polymers and promising the development of high efficiency red light emitting polymer.

4. Acknowledgement

We gratefully acknowledge financial support from the Center for Advanced Functional Polymers through Korea Science and Engineering Foundation (KOSEF).and BK 21.

5. Reference

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