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A NOVEL BRIGHT BLUE ELECTROLUMINESCENT POLYMER: POLY[4,4'-BIPHENYLENE-α-(9",9"-DIHEXYL- 3-FLUORENYL) VINYLENE]

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SUMMARY: Poly[4,4'-biphenylene-α-(9",9"-dihexyl-2-fluorenyl)vinylene] (PBPHFV) was synthesized by nickel catalyzed coupling reaction of 1,2-bis(bromophenyl)-1-(9",9"-dihexyl-2-fluorenyl)ethene and characterized by spectroscopic methods and elemental analysis. PBPHFV is soluble in common organic solvents. The weight average molecular weight (Mw) of PBPHFV is about 15000. PBPHFV showed good thermal stability as weight loss was less than 5 % on heating to 420 C under nitrogen atmosphere. The polymer film showed maximum absorption and emission at 370 nm and 485 nm, respectively. A bright blue electroluminescence (λ_{max} = 465nm, maximum intensity = 4116 cd/m^2) was obtained when the device was fabricated with the structure of ITO/PEDOT/PBPHFV/LiF/Al. The turn on voltage of the device was 4.3 V and the maximum efficiency was 0.22 lm/W. When the blend with PVK (PBPHFV : PVK = 1:5) was used as an emitting layer, the maximum brightness and efficiency of the device were 9342 cd/m^2 and 1.66 lm/W, respectively.

Introduction

Since light-emitting devices (LED) using conjugated polymers were first realized in the early 1990s1-2), a great number of different conjugated polymers suitable for LEDs have been investigated and developed. These conjugated polymers are especially attractive for use as the emitting layers in LEDs.

The most interesting conjugated polymers are poly(p-phenylenevinylene) (PPV)$^{1-6)}$, which is

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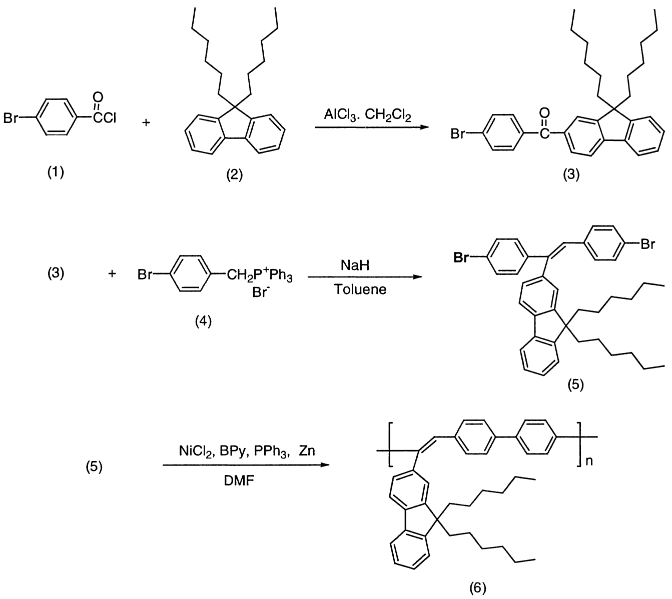
the first reported electroluminescent polymer, and PPV derivatives have several advantages as an emitting material; high thermal stability, good film quality, suitable color tunability, etc. However, it has low oxidative stability and some difficulties in processability and emitting blue color.

Poly(p-phenylene) (PPP)$^{7)}$, and its derivatives have also been extensively investigated for light emitting materials because they are thermally and oxidatively stable polymers. However, PPP derivatives exhibit low solubility, higher turn-on voltage and need low work function metal which is known to be decomposed easily in atmosphere. PPP derivatives are intrinsically violet-blue emitter to have some difficulties in color tunability.

Solubility, oxidative stability, low turn-on voltage, and color tunability (especially blue emission) are ideal properties for conjugated polymer used in LEDs. Moreover, good thermal stability is needed because of the heat generated when current is passed through the device.

One idea we kept thinking was how we could synthesize a blue-light-emitting conjugated polymer having advantages of PPP and PPV. It was, of course, extremly challenging to achieve. We, therefore, initiated synthesizing poly(biphenylenevinylene) (PBPV) derivatives, which are composed of alternating PPP and PPV units. On the basis of PBPV, our research also involved introducing substituents into vinyl bridge, giving steric interaction between the side groups and the adjacent phenyl ring. The steric hindrance imposed by the side groups offers a viable route for the design of PBPV with blue emission by controlling the conjugation length. Steric interaction may cause twisting of the polymer chain which reduces the effective conjugation length. In general, compounds that have shorter conjugation lengths have a higher photolominescence (PL) quantum yield. Introducing pendant groups attached to a vinyl bridge leads to enhance the solubility and oxidative stability of resulting polymers with respect to unsubstituted PPV. We recently synthesized several blue-light-emitting PBPV derivatives by taking advantages of these concepts given above$^{8)}$.

In this article, we describe the synthesis and application in LEDs of a new soluble blue-light-emitting PBPV derivative, poly[4,4-biphenylene-α(9”,9”-dihexyl-3-fluorenyl)vinylene] (PBPHFV). It was found that poly(9,9-dihexylfluorene)$^{9\text{-}12)}$ greenish blue emitter, has superior photo- and electroluminescent properties as well as good solubility. We took advantages of this component 9,9-dihexylfluorene moiety as pendant group at vinyl bridge. A large pendant group, 9,9-dihexylfluorene moiety, could lead to enhance the solubility of resulting polymer and shorten the effective conjugation length which results in bright blue-emission.



Scheme 1

Results and Discussion

The synthetic approach to this polymer is outlined in Scheme 1. The polymer was prepared by nickel-catalyzed coupling reaction. The polymer structure shown is consistent with the elemental analysis and the spectroscopic data from ^{1}H-NMR and FT-IR. The obtained polymer was readily soluble in common organic solvents. The weight average molecular weight of the polymer, as determined by size-exclusion chromatography using polystyrene standards, was Mw = 15500 (PDI = 1.5). The thermal gravimetric analysis (TGA) thermogram of the polymer shows that the polymer has good thermal stability up to 420 °C. Fig. 1 shows the UV-vis. absorption and photoluminescence of solid film, and electroluminescence spectrum which was obtained from ITO/PEDOT/PBPHFV/LiF/Al single layer device. The

UV-vis. spectrum of the polymer film showed maximum absorption and absorption edge are about 370 and 450 nm, respectively. It is 60 –70 nm blue shifted as compared with those of PPV13). This shift is a result of ineffective conjugation because of the strong steric hindrance between large side chain, (9,9-dihexylfluorene) and phenyl ring. The PL spectrum of a solid film of PBPHFV has a maximum peak at 485 nm, indicating greenish blue emission. However, maximum emission of electroluminescence was observed at 465 nm which is blue-shifted from that of PPV by 65 – 75 nm. As mentioned previously, this blue emission may be explained by short conjugation length due to steric hindrance. The introduction of bulky side group, 9,9-dihexylfluorene, into vinyl bridge led to disturb the coplanarity, which reduced the effective conjugation length.

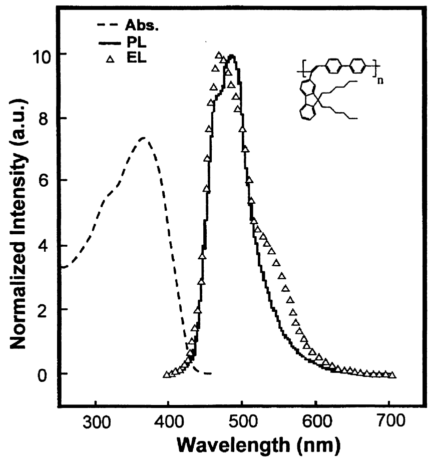


Fig. 1: UV-absorption, photoluminescence and electroluminescence spectra of PBPHFV

EL device prepared from the PBPHFV by using PEDOT as buffer layer, aluminum as cathod, and LiF as insulating layer showed a turn-on voltage of 4.3 V (0.089 mA/cm^2), efficiency of 0.22 lm/W (45 cd/m^2, 5.8 V, 0.011 A/cm^2), and maximum brightness of 4116 cd/m^2 (8.6 V, 1.18 A/cm^2). Because the poly(vinylcarbazole) [PVK] was known to serve several functions in the blend with emitting polymer material, the polymer was blended with the PVK$^{14-15)}$. The EL device prepared from the blend with PVK(PBPHFV:PVK =1:5) by using PEDOT as buffer layer showed a turn-on voltage of 7 V(0.014 mA), efficiency of 1.66 lm/W (41 cd/m^2, 14.8 V, 0.01 A/cm^2) and maximum brightness of 9342 cd/m^2 (20.6 V, 0.16 A/cm^2).

Conclusions

A new bright blue luminescent polymer, biphenylene vinylene containing bulky fluorenyl group, was synthesized. The obtained polymer was confirmed by various spectroscopic methods. The synthesized polymer was soluble and thermally stable. The maximum absorption and emission of polymer film showed at 370 nm and 485 nm, respectively. A bright blue electroluminescenece (λ_{max}) was observed by using the synthesized polymer as light emitting material. When the polymer was blended with PVK, the maximum brightness of device which has the structure of ITO/PEDOT/PBPHFV:PVK(1:5)/LiF/Al was 9342 cd/m^2 and the maximum efficiency was 1.66 lm/W.

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