Synthesis of Conjugated Polymers with Fluorene and Biphenylamine and Application to PLED Devices

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Abstract

Four kinds of copolymers with fluorene and biphenylamine units were synthesized by palladium-catalyzed polycondensation reaction. These polymers were characterized in terms of their UV/Visible and photoluminescence (PL) properties in solution and film state. These polymers were also studied as a hole transporting material in the polymer light emitting diode (PLED) devices.

1. Introduction

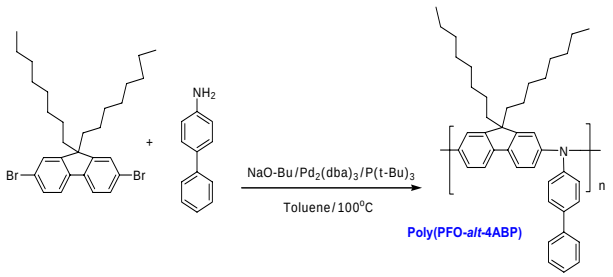
Recently conjugated polymers have attracted much attention from researchers for their potential applications to the large area organic light emitting diodes (OLEDs).[1,2] Several hole injection materials are available in the simple organic molecules, but polymer counter part is relatively few. Currently poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT/PSS) is used widely as the hole injection layer. But PEDOT/PSS suffer from its acidic nature which may cause degradation of the light emitting layer. Its poor electron blocking property is not favorable for the efficient recombination of electrons and holes in the emitting layer.[3,4] It is sometimes required to add an interlayer with high LUMO energy level to prevent movement of electrons to the PEDOT/PSS layer.

In this paper, we synthesized new conjugated polymers with fluorene and biphenylamine uint in order to test as hole injection (HIL) /transporting layer(HTL) in the OLED devices. These polymers have their highest occupied molecular orbital (HOMO) energy level close to the work function of ITO.[5]

2. Experimental

Synthesis of Poly (PFO -alt-ABP)s

Poly(dioctylfluorene-*alt*-biphenylamine)s such as Poly(PFO-4ABP), Poly(PFO-2ABP), Poly(PFO-AABP) and Poly(PFO-TABP), abbreviated as B1, B2, B3 and B4 were synthesized according to the Pd-catalyzed polyconsensation reaction. As shown in Scheme 1, a mixture of dibromodioctylfluorene (3.6mmol) and biphenylamine (3.6 mmol) were dissolved in toluene (40 ml). Catalysts consisting of NaO-t-Bu (10.8 mmol), $Pd_2(dba)3$ (0.09 mmol) and $P(t\text{-}Bu)_3$ (0.55 mmol) were added to the monomer solution at room temperature and then stirred at 100˚C for 48hr. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (80ml) and the product was extracted with chloroform solvent. The organic fraction was concentrated and reprecipitated form $CHCl_3$/methanol several times. The product (B1) were filtered and dried in vacuum. Other polymers (B2-B4) were synthesized by similar process. Four polymers were obtained in 50~60% yield.



Scheme 1. Synthesis of Poly(PFO-*alt*-4ABP), B1

Fabrication of PLED.

Polymer light emitting diodes (PLEDs) with configuration of ITO/PEDOT:PSS /poly(PFO-*alt*-ABP)/ BCP / Alq3 / LiF/Al and ITO / poly(PFO-*alt*-ABP)/Alq3/LiF/Al were fabricated by spin coating and thermal evaporation method by using Sunic Plus 200 OLED system .

3. Results and Discussions

3.1 Physical Properties of Polymer

Conjugated copolymers were synthesized to test as hole injection and hole transport materials. As shown in Figure 1, four kinds of copolymers had aromatic amine linkages with fluorene and biphenyl unit.

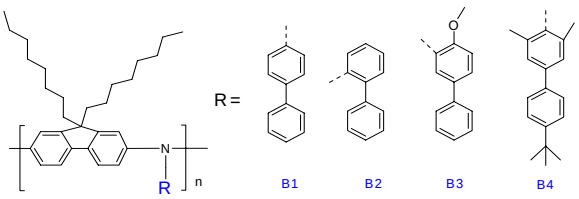
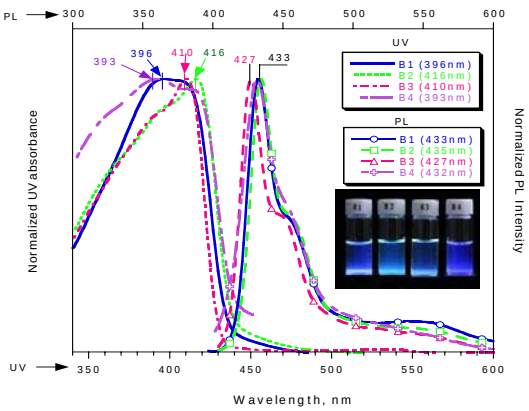
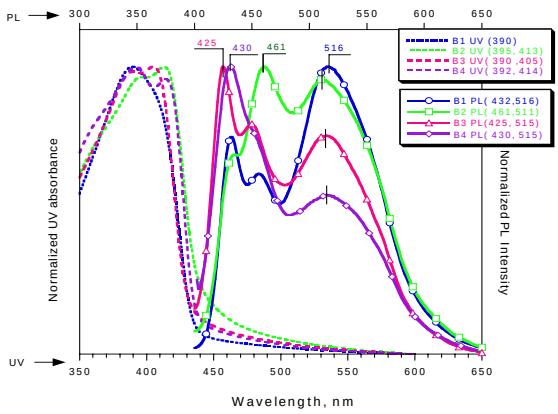


Figure 1. The Structure of Polv(PFO-alt-ABP)

The synthesized polymers showed good thermal stability in TGA and DSC measurement and have good film forming property. These polymers were characterized in terms of their emitting property both in the solution and solid states. As shown Figure 2, all the copolymers exhibited similar UV/vis absorbance and PL emitting spectra in solution state. In the solid film state, however, polymer B1 exhibited a large peak at about 516nm in addition to the peak at 427nm which was main PL peak in the solution state. The PL peak at 516nm was assigned to the eximers formed by biphenyl units in the solid film state. It was noted however that intensity of the eximer peaks decreased as more substituents were introduced in the biphenyl unit in the order of B1>B2>B3>B4.



(a)



(b)

Figure 2. The UV/vis absorbance and PL spectra of synthesized polymers (a) in solution state and (b) solid state.

3.2 Electro-optical Properties

The electro-optical properties of the synthesized copolymers are shown in Table 1. The quantum yields of the polymers were measured in toluene solution under the condition of UV absorption below 0.1 with the reference quantum yield(Φ_r) of 0.546 in quninine sulfate/1N aqueous H_2SO_4 solution at 365nm according to equation (1).

$$\Phi_B = \Phi r\ (ArF_B\ /A_BFr)\ (n_B^2/n_r^2) \quad \cdots \quad (1)$$

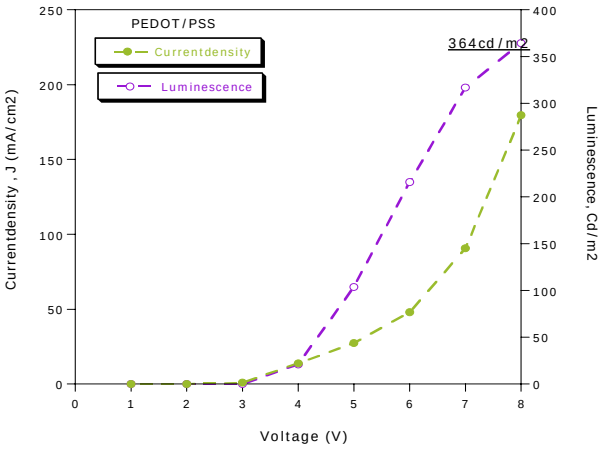
In eq.(1) A_B and F_B are UV absorption and Fluorescence intensity, n_B and n_r are refractive index of toluene (1.496) and 1N aqueous H_2SO_4 solution (1.399), respectively.

The polymer sample B4 exhibited highest quantum efficiency of 39% compared to the 21-28% of B1-B3 polymers. This high quantum efficiency of B4 polymer might be due to the bulky substituents in the biphenyl units which could reduce the nonradiative dissipation of excited energy by the effective prevention of free rotation of biphenyl units. This was in accordance with the low eximer peak of B4 polymer observed in the film state (Fig.2). It was also noted that the HOMO levels of the synthesized polymers were close to that of ITO electrode.

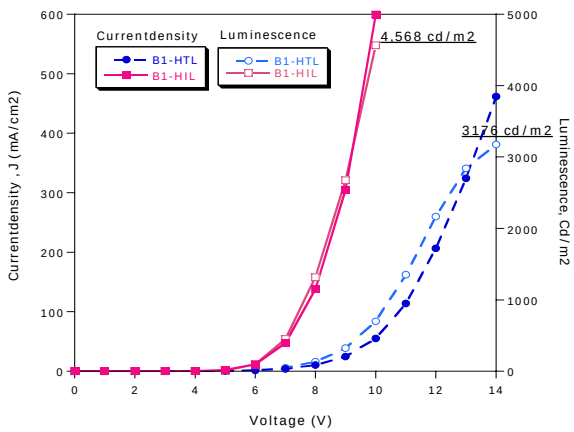
Fig.3 shows the I-V-L curves of the PLED devices with PEDOT/PSS as hole injection layer(HIL) (ITO/PEDOT:PSS/Alq_3/LiF/Al), the B1 polymer as hole transport layer(HTL) in the PLED device (ITO/PEDOT:PSS/B1/Alq_3/LiF/Al) and the B1 polymer as HIL/HTL layer in the PLED device (ITO/B1/Alq_3/LiF/Al). It was noted that B1 polymer exhibited higher luminance(4500 cd/m^2) than PEDOT:PSS(364 cd/m^2) when it was used as both HIL and HTL at same time.

Table 1. The electro-optical property of polymers.

Polymer	Mw	PDI	Solution (10^{-6} M $CHCl_3$) UV abs. (nm).	PL λmax (nm).	UV cutoff (nm)	Φs (%)	Band gap (eV)	HOMO (eV)	LUMO (eV)
B1	20,900	1.7	395	435	432	28	2.88	5.22	2.34
B2	8,600	1.5	416	435	439	26	2.81	5.10	2.29
B3	33,400	2.2	410	427	429	21	2.90	5.10	2.20
B4	4,700	1.3	385	432	434	39	2.86	5.08	2.22



(a)



(b)

Figure 3. I-V-L curves of PLED devices (a) PEDOT/PSS and (b) B1 polymer as hole injection/transporting layer.

4. Summary

The four fluorene-based copolymers with hole transporting biphenylamine units were synthesized by using palladium-catalyzed polycondensation reaction. These polymers were characterized in terms of their UV-Visible and photoluminescence(PL) properties both in solution and solid film state.

Polymer B4 exhibited high quantum yield in solution compared to other polymer samples. It was also observed that the synthesized polymer(B1) exhibited better hole injection/transport property than PEDOT:PSS hole injection material.

Acknowledgement

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5. References

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