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High Mobility Hole Transporting Polymers for Electroluminescence Applications

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A series of electroluminescent and conductive phenyl ring substituted poly(vinyl-N,N', diphenylnaphthylamine) (PXNPA, where X=H, OCH₃ and F) polymers was prepared. The polymers possess high hole mobility, excellent solubility and thermal stability. Their emission color, ionization potential (IP), quantum efficiency, glass transition temperature (T_g) and the efficiency and stability of the devices were all found to be related to the properties of the phenyl substituted side-group. As an example, the mobility for holes in Poly(4-MeONPA) is 10⁻⁵ cm²/V-s at room temperature compared to poly(N-vinylcarbazole) (PVK) at 10⁻⁷ cm²/V-s. It emits blue light at 450 nm; it has high thermal stability with onset decomposition temperature above 421°C; and a T_g of 132°C. A simple OLED device fabricated from the same polymer has a maximum luminance of 588 cd/m² at 175 mA/cm².
Keywords: Hole transporting polymer, Polymer OLED; Poly(vinyl-N,N',diphenylnaphthylamine).

1. Introduction

Organic light emitting diode (OLED) has gradually grown in popularity for making display devices.¹ It has the advantages of being brighter, lighter and no angular viewing limitation compared to conventional LCD. On the course to build a highly stable and cost-effective OLED, the design and careful characterization of the electroluminescent and charge transporting materials are essential for meeting the stringent manufacturing criteria.

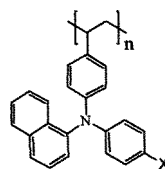
Recently polymer-based OLED has also attracted much interest because of the possibility of manufacturing large-area light-emitting display² at a lower cost. These is due to there are several significant advantages in material processing for polymeric materials over small organic molecules. For example, spin casting,³ inkjet printing,⁴ and using flexible substrates,⁵ are techniques that could make mass production of novel display devices possible at a lower cost.

In our previous research, we have investigated a series of hole transporting model compounds including N-(4-methoxyphenyl)-N'-phenyl-1-naphthylamine (4MeO-1NPA).⁶ It was found to be a blue light emitting dye with high hole mobility. However, low melting temperature (T_m) at 120°C make it undesirable for fabricating stable devices under high operating current. As a result, the same series of small molecules was further modified to prepare a series of NPA-based side chain polymers with improved thermal stability yet retaining the same mobility and emission characteristics.

2. Experimental

The chemical structure of PXNPA is shown in

Fig. 1(a)



where X = -H (P01)
-MeO (P02)
-F (P03)

Fig. 1(b)

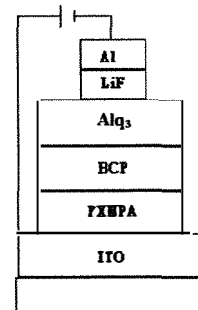


Fig. 1. (a) The chemical structure of P-XNPA, where X = H, OCH₃, F (b) Structure of organic EL devices using P-XNPA as the hole transporting layer and light emitter.

Fig. 1(a). The polymers were synthesized in 4 reaction steps with high yield. The preparation sequence began with a modified Ullmann condensation followed by a Vilsmeier formylation and then a Wittig coupling. Finally, the polymers were prepared by free radical solution polymerization of the monomers. The products were purified by reprecipitation twice in acetone/tetrahydrofuran (THF) and characterized by ¹H-NMR and IR. In the fabrication of OLED test devices, indium-tin oxide (ITO) coated glass slides (72 ohm/sq) were used as the substrate. They were subject to standard ultrasonic solvent cleaning and ultra-violet ozone treatments prior to high vacuum evaporation.⁷⁻⁸ The OLED device structure is shown in Fig. 1(b). The polymer thicknesses were ca 100 nm. Luminances of all devices were measured by a photometer (International Light, IL1400A) and checked by a

Minolta spot photometer (Model LS110). The thicknesses of the organic layer were calibrated by a stylus profilometer. The HOMOs were measured by cyclic voltammetry using ferrocene as standard in THF. The bandgap energy was calculated from the solution absorption spectrum edge. The mobility of the polymers and their model compounds were measured by a time of flight (TOF) method. Details of the TOF setup had been reported in elsewhere.⁹

3. Results and Discussion

Polymers with molecular weight as high as 200,000 have been prepared and they are all soluble in common organic solvents such as THF, toluene, chlorinated solvents with the exception of alcohols and acetone. Figure 2 shows the EL spectra of the devices. The narrow

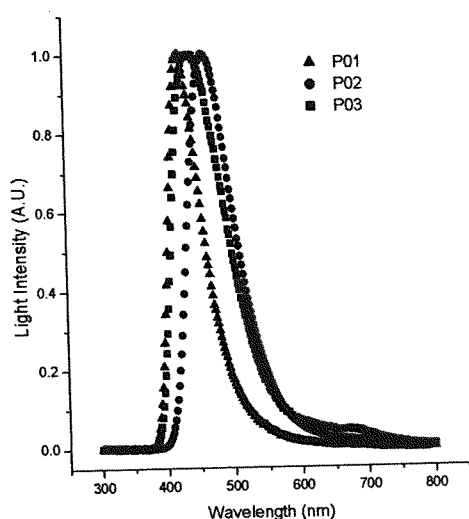


Fig. 2. EL spectra of the three polymer devices.

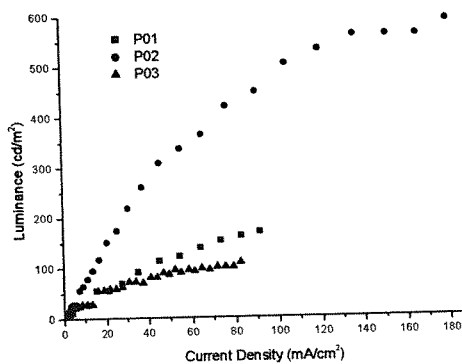


Fig. 3. Luminance-current characteristics of ITO/PXNPA/BCP/Alq₃/LiF/Al devices

Table 1. Device properties for the PXNPA

	EL CIE	EL λ_{max} (nm)	FWHM (nm)	L_{max} (cd/m ²)	Turn on Voltage (V)
P01	0.161, 0.079	424	56	170	12
P02	0.160, 0.136	450	66	588	16
P03	0.175, 0.143	434	86	110	13

peak-width of the EL spectra is characteristic of the side chain polymers since there are no conjugation between emitting moieties. The polymer OLED emitted in the deep blue region ranging from 424–450 nm due to the employment of a hole blocking BCP (bathocuproine) layer. The emission maxima were similar to those of the respective model compounds and the strongly electron donating methoxy side-group (P02) produced the largest red-shift from the unsubstituted 4H-1NPA.⁶

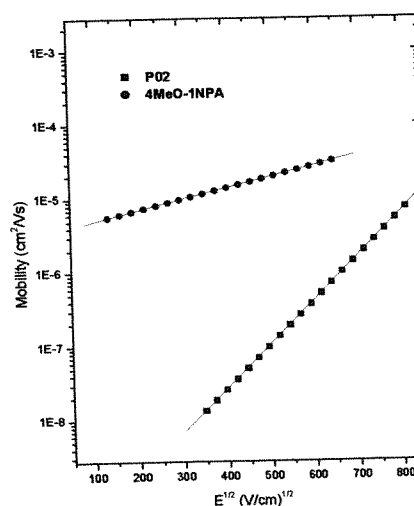


Fig. 4. The hole mobility of the polymer (P02) and respective model compounds at 289 K against the square root of the electrical field $E^{1/2}$. The model compounds were mixed with polycarbonate (PC) in a ratio of 7:3 by weight.

The luminance of the polymer-based devices was much higher than those based on the model compounds mainly due to improved thermal stability. Best result was achieved by P02, which has a maximum luminance of 588 cd/m² at 175 mA/cm². (see Fig. 3) The electron-donating methoxy group (P02) gave a higher luminance than the electron withdrawing fluoro group (P03) and is in proportion to their quantum efficiency in solution. The quantum efficiencies for P01, P02 and P03 were 0.35, 0.51 and 0.16 respectively. The luminance efficiency and stability increased according to the order F < H < MeO.

Figure 4 shows hole mobility of the model compounds (4MeO-1NPA) and the same polymer (P02) in the series. The mobilities measured were comparable to a

tetraphenyldiaminobiphenyl (TPD) containing side-chain polymers with 10^{-5} cm²/V-s at an applied field of 1.6×10^5 V/cm.¹⁰ In analyzing the mobility for the different polymers and their respective model compounds, it was shown that mobility was affected by the electronic properties of the substituent side-group. Weaker dipolar moment generally favors the transport of charges. At 289K, the best hole mobility was found for the unsubstituted 4H-1NPA which has values in the range of $0.5 - 2 \times 10^{-4}$ cm²V⁻¹s⁻¹ and is in the same order of magnitude to 4,4'-bis[(1-naphthylphenyl) amino]biphenyl (NPB) (5×10^{-4} cm²V⁻¹s⁻¹).¹¹ The mobility of the substituted NPA compounds (both 4MeO-1NPA and 4F-1NPA) was slightly lower in the range of 1×10^{-5} cm²V⁻¹s⁻¹. However, for P02, it was found to have an even stronger field dependence and weaker mobility than that of its small molecule analog (4MeO-1NPA) which was suggested due to an increase in energetic disorder. Detailed analysis on the mobility data will be reported later.

The glass transition temperatures for P01, P02 and P03 were 162, 132 and 162°C respectively and were substantially higher than the value for some small molecule hole transporting compounds commonly used (e.g. Tg for TPD is 60 °C). The lower T_g for P02 is due to the rather flexible methoxy side-group. The onset degradation temperature (T_d) for the polymers under nitrogen environment was all above 400°C. The T_d for P01, P02 and P03 were 451, 421 and 450 respectively.

The ionization potential (HOMO) for the polymers was measured and report in Table 2. It is interesting to find the IP value can be fine tuned by the substituted side-group. The results matched trends indicated from

Table 2. Redox potentials of the polymers

	Model compounds		Polymers		
	(eV)		(eV)		
	HOMO	LUMO	HOMO	LUMO	
H-NPA	5.363	2.118	P01	5.276	2.082
MeO-NPA	5.222	2.088	P02	5.146	2.113
F-NPA	5.382	2.136	P03	5.314	2.314

a previous report.¹² The electronic donating group usually reduces the IP value while a withdrawing group increases it. The IP for the polymers increases in the order MeO < H < F.

4. Conclusions

In conclusion, a series of side-chain hole transporting polymers has been prepared by facile synthetic procedures. Their hole mobilities are in the same order of magnitude compared to other commonly used hole transporting compounds. The polymers are highly soluble and have excellent thermal

stability. A series of blue light emitting OLED was prepared from the polymers. The, emission characteristics, efficiency, stability and IP were all found to be affected by the electronic properties of the substituent side-group.

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