Synthesis and Electroluminescence of Novel Copolymers with Charges Transporting Moieties

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The synthesis of novel copolymers, in which the electron transporting unit (oxadiazole), hole transporting unit (carbazole) and emitter (naphthalimide) are incorporated into one copolymer, has been reported. It was demonstrated that EL spectra of device made by these copolymers has a broad luminescent spectrum with range of 450-650 nm, which can be quantified in CIE coordinates as x = 0.32 and y = 0.37.

Much attention has been devoted to the polymeric electroluminescent (EL) devices due to their potential for application in display technology.[1-2] The conjugated backbone presents problems for synthesis and processing because it tends to make the polymer very rigid and hence insoluble. There are two main approaches to overcoming this problem:[3] to form a non-conjugated precursor polymer and then converted *in situ* to the conjugated polymer; and to make a soluble conjugated polymer by the addition of lipophilic soluble linkers or side groups. A disadvantage of precursor route polymers is that there is some evidence that by-products from the conversion from precursor to conjugated polymer can damage electrodes. One of the disadvantages for soluble conjugated polymers is that it can be more difficult to prepare multilayer devices by solution processing. In the letter, we report the synthesis of novel copolymers P(NA-VC) (shown in Figure 1) used for EL devices. In such copolymers, the electron transporting unit (oxadiazole moiety, OXZ), hole transporting unit (carbazole, VC) and emitter (naphthalimide, NA) are incorporated into one copolymer. These copolymers are organic solvent soluble and can be used to make uniform thin films for single layer structure EL device by some standard methods of processing involve spin or blade coating. In previous work, we have studied the properties of EL devices using novel dyad or triad emitting compounds.[4,5] Such assemble molecules with three functions did indeed obviously increase luminous efficiency of EL device.

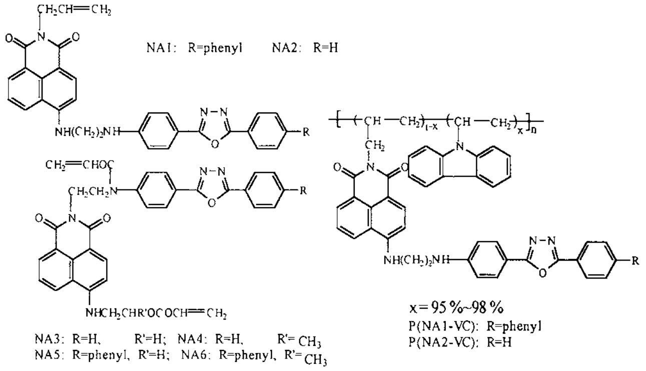

Figure 1. Structures of monomers and copolymers P(NA-VC).

The series of monomers (NA1-6) were synthesized in our laboratory and their chemical structures were confirmed by ^{1}H NMR and MS spectra.[6] The data of absorption and fluorescence spectra of these monomers in THF are shown as follows: NA3: λ_{max}^{ab}/nm: 323.2, 427; λ_{max}^{fl}/nm: 503. NA4: λ_{max}^{ab}/nm: 322.6, 427.4; λ_{max}^{fl}/nm: 505. NA5: λ_{max}^{ab}/nm: 330.4, 427.2; λ_{max}^{fl}/nm: 501. NA6: λ_{max}^{ab}/nm: 332.1, 427.3; λ_{max}^{fl}/nm: 500.4.

The general preparation of copolymer P(NA1-VC): NA (0.10 g) and N-vinyl carbazole (1.0 g) were dissolved in toluene (10 ml), followed by sufficiently degassing by argon gas, adding benzoyl peroxide (10 mg), agitating the mixture at 80 °C for 12 h, cooling, dropwise adding the solution into methanol (150 ml), repeating this procedure three times, to obtain greenish yellow solid copolymer P(NA-VC) 420 mg. Using the standard line method of UV-Vis spectra, the content of NA derivative segments in P(NA1-VC) was 2.3% (mol/mol). The average molecular weight determined by GPC was about 100000. The data of absorption and fluorescence spectra of the copolymer P(NA1-VC) in THF: λ_{max}^{ab}/nm: 289, 330, 440; λ_{max}^{fl}/nm (excited at 330 nm): 376, 415 (shoulder), 498; λ_{max}^{fl}/nm (excited at 400 nm): 501, and in thin film: λ_{max}^{ab}/nm: 290, 340, 440; λ_{max}^{fl}/nm (excited at 340 nm): 412, 495; λ_{max}^{fl}/nm (excited at 440 nm): 503. Two typical EL devices are composed of a thin copolymer layer sandwiched between two electrodes: a) glass/ ITO/ copolymer (P(NA1-VC))/ Mg:Ag; b) glass/ ITO/, PEDT/ PSS/ copolymer (P(NA1-VC))/ Mg:Ag. The copolymer was dissolved in CH_2Cl_2 (1%). The solution was filtered (0.45 µm) and deposited onto a substrate by spin coating. In case a) the substrate was cleaned ITO (Balzers 255), in case b) it was ITO with a 50 nm layer of PEDT/PSS (Bayron P, Bayer) that is used to modify the surface of ITO. The copolymer layer thickness in both cases is 90 nm. The cathode (0.28 cm^2) of EL device in this work was deposited on the top of the copolymer by thermal co-evaporation of Mg and Ag with rate close to 10:1.[7]

Figure 2 demonstrates the normalized EL spectra of device a, which can be quantified in CIE coordinates as x = 0.32 and y = 0.37 (recorded at 25 V). The device has a broad luminescent spectrum (nearly white color) that spans the range of 450-650 nm with a peak at *ca.* 510 nm. The peak corresponds to the emission of naphthalimide, which means that naphthalimide plays main role in EL emission although that the content of naphthalimide moiety in the copolymer is very low. When the content of naphthalimide segment was relatively high in our previous study,[6] this kind of copolymer has a relative narrow EL spectra with the same peak at *ca.* 510 nm. The characteristics of EL devices made with those copolymers, in which the content of NA unit is high (6.3%-12.6%), showed that the charge carriers injection balance should be improved by means of blending the copolymers in PVK (up to 40% v/v). From the fluorescence spectra of the copolymer P(NA1-VC) in THF, the emission of the carbazole (376 nm) as well as the oxadiazole segments (415 nm) is observed when excited at 330 nm. The absorption and emission maxima of *N*-ethyl-4-dimethylamino-1,8-naphthalimide in THF are 407 nm and 508 nm, respectively. The emissions of

OXZ and VC units with high concentration ratio were obviously partly quenched in the operation of the device. The EL emission characteristic of this kind of copolymer is similar with that of the organic dyad or triad molecules.[5,6] This can be explained in the following way: when the EL device is operated, electrons are injected from the Mg:Ag cathode (*ca.* -3.7 eV) into the π^* orbital of the OXZ moiety (LUMO level for PBD is *ca.* -2.50 eV)[1] and holes are also injected from the anode of ITO (-4.6 eV) into the π orbital of the VC moiety (HOMO level for PVK is –5.80 eV).[2] The intramolecular electron and hole transfers thus occur. The electrons are transferred to the LUMO level (-3.02 eV) of NA moiety from OXZ, and the holes are transferred to the HOMO level (-5.78 eV) [8] of NA moiety from VC moiety, respectively. The holes and electrons then recombine in the NA moiety to form exciton that undergoes radioactive decay resulting in electroluminescence. Therefore, a main characteristic emission of the NA moiety is present in the EL spectrum for the copolymers. The VC moieties in the copolymer facilitate the injection of holes from the electrode and act as electron-blocking moiety. On the other hand, the OXZ moieties in the copolymer facilitate the injection of electrons from the electrode and act as hole-blocking moiety. Considering the complication of doping and the possibility of the interface exciton quenching between layers in multilayer device, this may be a novel route to design new emitting materials and be hopeful to fabricate single layer EL devices to simplify the procedure.

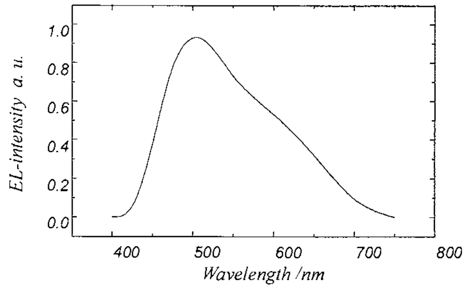

Figure 2. EL spectrum of device a: ITO/P(NA1-VC)/ Mg:Ag.

Figure 3 illustrates the current *vs.* voltage (I-V) and brightness *vs.* voltage (B-V) characteristics of the EL devices. The maximum brightness of the two EL devices is 25 cd/m^2 when driving voltage is 20 V. The brightness increases superlinearly upon the voltage, just like the current. It should be noted, in case of device a, a pronounced dependence on the curve history was found. Fresh sample showed a high device current at low voltages, and the high current vanished when a certain voltage (about 10 V) was reached (as shown in Figure 3). For device b, we didn't observe such phenomenon. The reason for the difference in this case is not yet clear. The EL device made with P(NA2-VC) showed relative short operation lifetime. The I-V and B-V behavior were difficult to obtain repeatedly. The reason may be due to the trend of recrystallization of the OXZ segment (R= H) in P(NA2-VC) under applied voltage. It is astonish to us that the EL brightness is relatively low (only 25 cd/m^2). The purity of the copolymers affects seriously the operation lifetime of EL device. Another reason may due to the low concentration of emitter (naphthalimide) in copolymers.

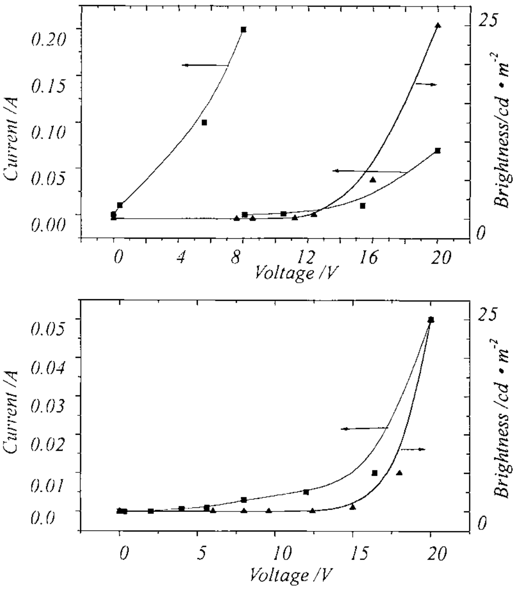

Figure 3. Current *vs.* voltage (I-V) and brightness *vs.* voltage (B-V) characteristics of device a (upper) and device b (bottom).

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References and Notes

1 F. Cacialli, X.-C. Li, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Synthetic Metals*, **75**, 161 (1995).
2 M. Hamaguchi and K. Yoshino, *Jpn. J. Appl. Phys.*, **35**, Part 1, No.9, 4813 (1996).
3 P. L. Burn and I. D. W. Samuel, *Materials Today*, **1**, 3 (1998).
4 W. J. Ni, J. H. Su, and H. Tian, *Chem. Lett.*, **1997**, 101.
5 H. Tian, W. H. Zhu, and K. C. Chen, *Synthetic Metals*, **91**, 229 (1997).
6 W.H. Zhu, C. Hu, K.C. Chen, and H. Tian, *Synthetic Metals*, **96**, 151 (1998).
7 D. D. C. Bradley, *Synthetic Metals*, **54**, 401 (1993).
8 K. Utsugi and S. Takano, *J. Electrochem. Soc.*, **139**, 3610 (1992).