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DOPED ORGANIC LIGHT-EMITTING DIODES BASED ON RANDOM COPOLYMERS CONTAINING BOTH HOLE AND ELECTRON TRANSPORT GROUPS

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ABSTRACT

Doped organic light-emitting diodes (OLEDs), such as PVK containing the electron transport molecule PBD and molecular dyes, have demonstrated three-color capabilities and efficiencies over 1%, but there are concerns about reliability due to recrystallization of the small molecule PBD. In this work we describe the incorporation of both hole and electron transport groups into a single copolymer to avoid recrystallization and phase segregation (which could occur if two separate polymers were used) as well as the application of such copolymers in dye-doped OLEDs. The polymers were synthesized through free radical copolymerization of the electron-donating monomer N-vinylcarbazole (NVK) with the electron-withdrawing monomer 2-(4-tert-butylphenyl)-5-{4-[(4'-vinyl)phenylmethoxy] phenyl}-1,3,4- oxadiazole (BVO). The radical reactivity ratios of the two monomers were estimated to be r_{NVK}=0.052 and r_{BVO}=12. The copolymers are transparent in the visible region, homogeneous as characterized by both GPC and DSC, and have good thermal stability. External quantum efficiencies of 0.07%, 0.3% and 0.4% were achieved in LEDs with device structures of ITO/COP:C47/Mg:Ag, ITO/COP:C6/Mg:Ag and ITO/COP:NR/Mg:Ag, respectively, where COP stands for copolymer, C47 for Coumarin 47, C6 for Coumarin 6 and NR for Nile Red. The introduction of the oxadiazole group balances the injection of holes and electrons by decreasing the hole injection and transport ability and enhancing the electron injection and transport ability of the copolymers relative to PVK.

INTRODUCTION

Organic and polymer light emitting diodes (LEDs) have achieved great progress in the last decade. However, improvements in device stability and efficiency are still desired. There are several approaches to improve device efficiency. One way is to synthesize materials with higher photoluminescence efficiency [1]. Another way is to improve the injection of holes and electrons. A favorable balance for charge injection and transport of both carriers is needed for high efficiency. This can be realized either by device structure or material property design. The use of transport layers in devices has proven effective in achieving high efficiency. Low molecular weight oxadiazoles are frequently used as an electron injection and transport layer. Thin films of these oxadiazoles are amorphous but have a strong tendency to recrystallize, which is thought to be one of the reasons for the short device lifetime [2]. An alternative is to employ a guest-host system in which oxadiazoles are embedded in a polymer matrix. In this way, a single-layer device can be made with high efficiency, simplifying fabrication. For example, dye-doped organic LEDs based on a blend of the hole transport polymer poly(N-vinylcarbazole) (PVK) and the electron transporter 2-(4-tert-butylphenyl)-5-biphenyl-1,3,4-oxadiazole (PBD) have demonstrated three-color capabilities and efficiencies about 1% [3,4]. But there are also concerns about reliability due to recrystallization of the small molecule PBD, which may then result in phase separation. This can be overcome by covalently attaching the oxadiazole groups to the polymer chain. In this work we describe the incorporation of both hole-transport carbazole and electron-transport oxadiazole groups into a single copolymer and its application in dye doped LEDs. Fig. 1 shows the structures of the monomers and copolymers (COPs); the oxadiazole monomer (BVO) is very similar in structure to PBD, and so should show similar electronic properties, but BVO contains a polymerizable styryl group at one end so as to allow easy incorporation into a polymer by free-radical copolymerization.

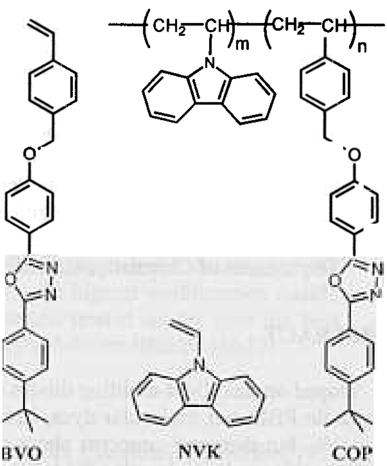

Fig. 1. Molecular structures of the monomers and copolymers

EXPERIMENT

Materials Synthesis and Characterization

NVK was purchased from Aldrich. The detailed synthesis of BVO will be published elsewhere [5]. Polymerization was carried out in tetrahydrofuran (THF) and azobisisobutyronitrile (AIBN) was used as initiator. The copolymers were purified by repeated reprecipitation from THF into methanol. Compositions of the copolymers were determined by UV-vis spectral analysis using an HP 8452A diode array spectrometer. Molecular weights of the copolymers were determined by gel permeation chromatography (GPC), using a Waters 590 pump, 60 cm PLgel 5μ MIXED-C column, a Waters 490E programmable multiwavelength UV detector, and THF as the solvent. Reported molecular weights are relative to narrow-distribution polystyrene standards. Glass transition temperatures (*T*g) of the copolymers were measured using a Perkin-Elmer DSC7 differential scanning calorimeter at a scan rate of 10 °C/min.

Device Fabrication and Testing

ITO substrates were precleaned ultrasonically and were treated with oxygen plasma prior to spin coating of the polymer layer [4]. The dye-doped polymer layer (either PVK, PVK:PBD, or copolymer) was spin coated onto the ITO substrate from a 28 mg/ml solution (total solids) in 1,2-dichloroethane at 3500 to 4000 rpm in a nitrogen glove box. This produced a polymer film thickness of 700-1000 Å as measured by stylus profilometry. Then a layer of Mg:Ag (10:1) with thickness of 1000 Å was evaporated at a pressure of 2×10^{-5} Torr. The active area of the device was about 8 mm^2. A layer of Ag with thickness of 1000 Å was then deposited as a cap. For hole-only devices, a layer of gold was evaporated instead of the Mg:Ag and Ag layers. The current - voltage and photocurrent - voltage characteristics were measured on a HP 4145B Semiconductor Parameters Analyzer and calibrated Si photodiode system under nitrogen.

RESULTS

To have good control over the copolymer composition, the radical reactivity ratios of the two monomers were determined by running several small-scale polymerizations with varying ratios of NVK:BVO in the monomer feed. Table I gives the compositions of the monomer mixture and the corresponding copolymers formed in these small-scale polymerizations. The compositions of the copolymers were determined using the molar extinction coefficients for the two parent homopolymers [5]. Based on these data, the reactivity ratios of NVK and BVO were estimated to be $r_{NVK} = 0.052$ and $r_{BVO} = 12$ using the Fineman-Ross graphical method [5]. We then ran two large-scale polymerizations to produce copolymer batches for device fabrication; Fig. 2 shows the UV-visible spectra of these two copolymers (COP1 and COP2). The copolymers have no absorption above 350 nm and so are completely transparent in the visible range. This is favorable for an OLED matrix material used in OLEDs because absorption of the emitted light by the matrix will lower the quantum efficiency and change the color of the emission, which could complicate the realization of a color display. The mole and weight fractions of NVK, F_{NVK} and W_{NVK}, are 0.69 and 0.51 in COP1 and 0.83 and 0.70 in COP2. Since the reactivity ratios for the two monomers are far from unity, the instantaneous composition of the copolymer drifts quickly with increasing conversion. The homogeneity of the copolymers was studied by DSC and GPC.

Table I. Monomer feed and copolymer compositions.

Monomer Feed (f_{NVK})	0.9489	0.8952	0.7975
Mole Fraction in Copolymer (F_{NVK})	0.54	0.36	0.23
Conversion Degree (x)	0.069	0.077	0.087

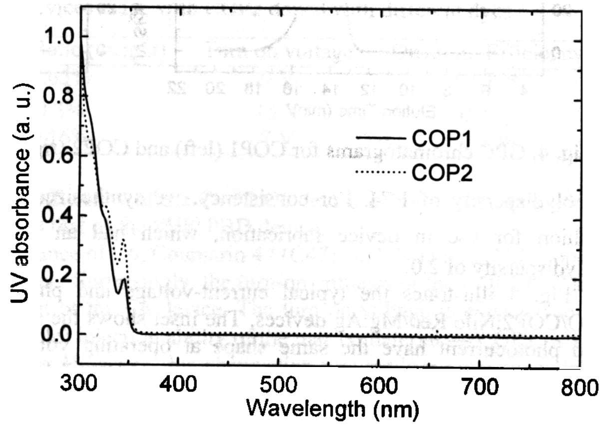

Fig. 2. UV-Vis absorption spectra of the copolymers.

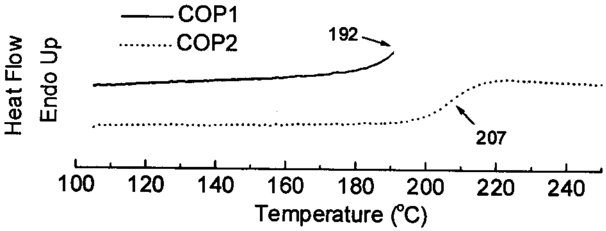

Fig. 3. DSC traces for COP1 and COP2.

Fig. 3 shows the DSC traces for COP1 and COP2. Both have only one narrow *T*g, indicating homogeneity. The *T*g values for COP1 and COP2 are 192 and 207 °C, respectively. The copolymers show no sign of degradation after being heated to 250 °C, indicating good thermal stability. Fig. 4 shows the GPC chromatograms for COP1 and COP2. To study the homogeneity of the copolymers, the chromatogram was measured simultaneously at 254 nm (absorption of benzene ring), 310 nm (strong BVO absorption, minimal PVK absorption) and 344 nm (PVK peak absorption, almost no BVO absorption). The chromatograms detected at different wavelengths superimpose with each other perfectly after normalization, confirming that the copolymers are homogeneous. The polystyrene-equivalent weight-average molecular weight of COP1 is $\overline{M_w} = 59600$ g/mol, and the polydispersity is 1.85; for COP2, $\overline{M_w} = 94900$ g/mol, with

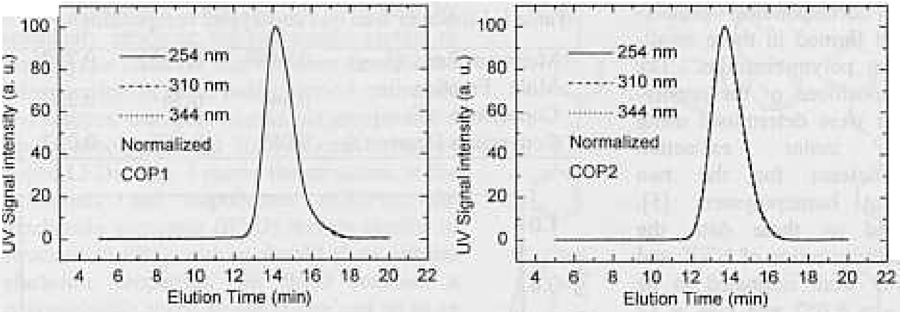

Fig. 4. GPC chromatograms for COP1 (left) and COP2 (right) detected at 254, 310 and 344 nm.

a polydispersity of 1.74. For consistency, we synthesized a PVK homopolymer in the same fashion for use in device fabrication, which had an apparent $\overline{M_w}$=33800 g/mol and a polydispersity of 2.0.

Fig. 5 illustrates the typical current-voltage and photocurrent-voltage characteristics of ITO/COP2:Nile Red/Mg:Ag devices. The inset shows the same data on a log scale. The current and photocurrent have the same shape at operating voltages, indicating balanced hole and electron injection. The device turn-on voltage is about 7 V, defined as the voltage at which the photocurrent begins to increase superlinearly, as shown in the inset.

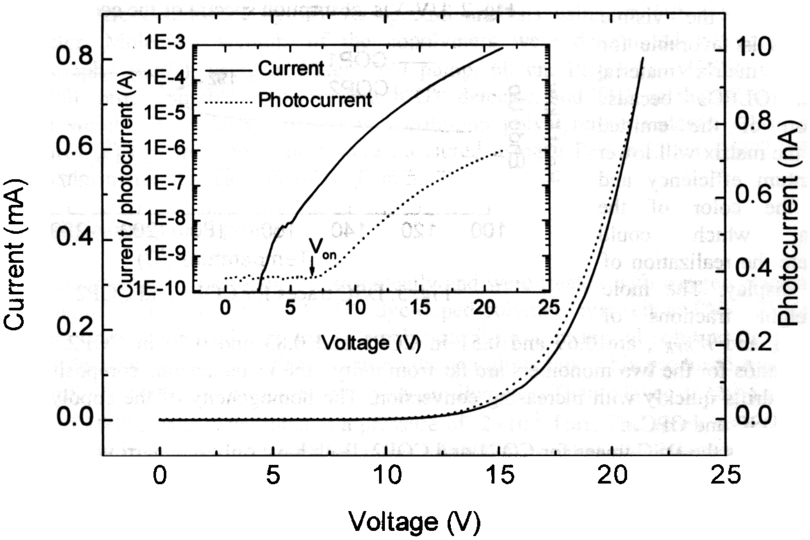

Fig.5. Typical current- and photocurrent-voltage characteristics of ITO/COP2:NR/Mg:Ag .

Table II compares the performances of PVK, PVK:PBD (100:40 by weight) and COP2 devices, all doped with Coumarin 6 (C6). The turn-on voltage of the COP2 device is higher than that for the PVK and PVK:PBD devices. This may be caused by the lower hole mobility of the copolymer, since the turn-on voltage of an OLED is determined by injection of majority carriers

Table II. Performance of devices made with different polymers doped with 0.3 wt% C6

Device structure	Turn-on voltage (V)	Quantum Efficiency
ITO/PVK:C6/Mg:Ag	8	0.2 %
ITO/PVK:PBD:C6/Mg:Ag	13	0.45 %
ITO/COP2:C6/Mg:Ag	16	0.3 %

Table III. Performances of devices made with COP2 doped with different dyes

Device structure	Doping Ratio (weight)	Turn on voltage	Quantum Efficiency
ITO/COP2:C47/Mg:Ag	0.65%	9 V	0.07 %
ITO/COP2:C6/Mg:Ag	0.3%	15 V	0.2 %
ITO/COP2:NR/Mg:Ag	0.16%	7 V	0.4 %

[6]. However, the external quantum efficiency of the COP2:C6 device is higher than that of the PVK:C6 device, though not as high as that of the PVK:PBD device.

Table III summarizes the performance of C6, Coumarin 47 (C47) and Nile Red (NR) doped COP2 devices, all fabricated in parallel. Surprisingly, the turn-on voltages of the COP2:C47 and COP2:NR devices are lower than that of the C6 device. The turn-on voltage is expected to be determined by the majority carrier (hole) injection ability of the matrix material — COP2, which is the same for all of the three devices. However, this observation was made for two separately-fabricated batches of devices; we are currently working to clarify this phenomenon. The external quantum efficiency of the NR device is twice that of the C6 device, and six times that of the C47 device. This implies that the energy transfer between COP2 and NR is more efficient, in contrast to the results for dye-doped PVK:PBD devices, where the C6 doped device has the highest efficiency [4]. Further study on the origin of this difference is underway. Fig. 6 shows the electroluminescence (EL) spectra of C47, C6 and NR doped COP2 devices. They are identical to the photoluminescence (PL) spectra of the corresponding dyes (not shown here), meaning that device emission originates exclusively from the dyes. This shows that energy transfer from the matrix to the dyes is very efficient.

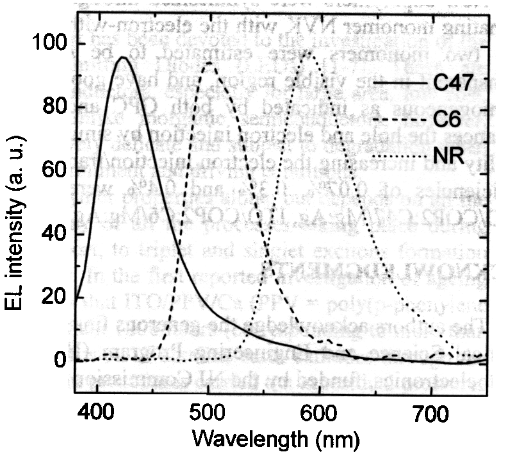

Fig. 6. EL spectra of ITO/COP2:dye/Mg:Ag devices.

To study the influence of the oxadiazole group on the hole injection and transport ability of the copolymer, dye-free polymer LEDs were made with ITO as the anode and Au as the cathode. Because the work function of Au is very high, it is expected that no electrons will be injected into the device. Therefore, the amplitude of the forward driving current can be used as an indicator of the hole injection and transport ability of the polymer films. Fig. 7 demonstrates the current-voltage characteristics of ITO/PVK/Au, ITO/PVK:PBD(100:40)/Au, ITO/COP1/Au and ITO/COP2/Au devices. The hole injection and transport ability of the polymer films decreases in the following order: PVK > PVK:PBD > COP2 > COP1. While the oxadiazole group is electron-transporting, it is also hole-blocking [7], so the incorporation of the oxadiazole groups into the polymer will increase the electron transport ability and decrease the hole transport ability of the copolymer. Since hole transport in PVK occurs by a hopping mechanism between carbazole groups [8], it seems reasonable that as the concentration of carbazole groups decreases, either through the addition of monomeric PBD or through copolymerization, the hole mobility will decrease. The PVK:PBD blend and COP2 have similar overall compositions (PVK weight fractions near 0.70), and indeed, the I-V characteristics for these two devices are grossly similar. The higher current carried in the PVK:PBD blend device may reflect the fact that, because the carbazole units are sticking together as a homopolymer, holes can hop between adjacent carbazole units along the chain, whereas in the copolymers this path is interrupted.

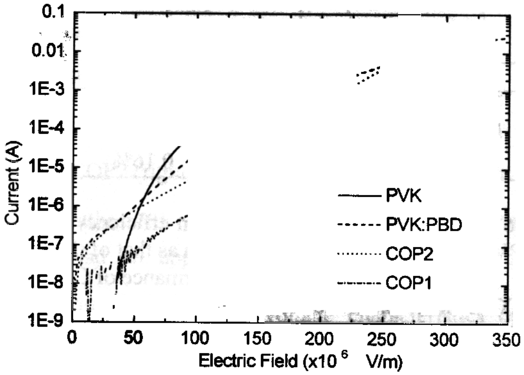

Fig. 7. I-V characteristics of ITO/polymer/Au devices.

CONCLUSIONS

New copolymers were synthesized through free radical copolymerization of the electron-donating monomer NVK with the electron-withdrawing monomer BVO. The reactivity ratios of the two monomers were estimated to be r_{NVK}=0.052 and r_{BVO}=12. The copolymers are transparent in the visible region, and have good thermal stability. The copolymers as made are homogeneous as indicated by both GPC and DSC. The introduction of oxadiazole groups balances the hole and electron injection by simultaneously decreasing the hole injection/transport ability and increasing the electron injection/transport ability of the copolymer. External quantum efficiencies of 0.07%, 0.3% and 0.4% were achieved in LEDs with device structures of ITO/COP2:C47/Mg:Ag, ITO/COP2:C6/Mg:Ag and ITO/COP2:NR/Mg:Ag.

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