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Binary solvent mixture-induced crystallization enhancement for a white emissive polyfluorene copolymer toward improving its electroluminescence

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The morphology of fluorescent polyfluorene (PF) derivatives has strong effects on their electroluminescent (EL) performance. Herein, the influence of processing solvents on the morphology of PF-based white emissive polymer and its correlation to the EL behavior is studied. It is found that the PF copolymer films prepared from chlorobenzene:toluene (CB:TOL) solvent mixtures show stronger tendency to form crystalline α phase PF upon thermal annealing than those prepared from pure TOL or CB solvents. The evaporation rate difference in solvent mixtures can assist in the formation of crystal nucleus and enhance the crystallinity of PF backbone after thermal annealing. The results also reveal that the solvent mixture-processed fluorescent PF-based white emissive polymer not only shows more efficient blue emission, but also more balanced electron and hole transport. Accordingly, both the white emission purity and the light-emitting efficiency of the light-emitting diodes based on PF-based white emissive polymer are greatly enhanced.

1. Introduction

White organic light-emitting diodes (WOLEDs) have drawn a lot of attention due to their promising applications in next-generation flat-panel display and solid-state lightings [1]. For solution-processed white polymer light-emitting diodes (WPLEDs), particular attraction is received owing to the combined advantages of simple device structure and cost-effective fabrication technologies, typically suitable for large-area manufacturing such as ink-jet printing or screen-printing methods [2,3]. Several strategies have been developed for WPLEDs, including all-polymer blends or polymer host-small molecule dopant systems, *etc.* [4]. However, these systems are suffered from potential phase separation, which is adverse to the required long-term efficiency and electroluminescent (EL) spectra stability [5]. Alternatively, WPLEDs based on single white emissive polymer (SWP) were developed, which have shown promising device efficiencies and EL spectra stability. These SWPs are typically composed of a wide band-gap polymer host, such as polyfluorene (PF), with small amounts of varied color chromophores covalently anchored onto it [2,6]. Because of its highly coplanar backbone, the PF film can be physically transformed into a variety of supramolecular structures (e.g. amorphous, crystalline (α and α′) phase, mesomorphic (β) phase, *etc.*) that have strong influence on its optoelectronic properties [7–13]. The morphology of the PF films is strongly dependent on the processing conditions, e.g., the solubility parameter of the solvent, the evaporation rate of the solvent, and the temperature of the post thermal annealing. For instance, the PF films show a tendency to crystallization in a poor solvation environment or low evaporation rate of solvent. Low temperature (<100 °C) annealing is helpful for β phase formation, while higher temperature annealing can induce the rearrangement from β phase to α phase in PF films [14,15].

Herein, we have studied the influence of different solvent conditions including toluene (TOL), chlorobenzene (CB) and CB:TOL solvent mixtures on the morphology of PF-based white emissive polymer and the EL performance of the resulted WPLEDs. Compared to those prepared from pure TOL or CB solvents, the white emissive PF copolymer films prepared from CB:TOL solvent mixtures show strong tendency to form crystalline α phase PF upon thermal annealing. The extent of PF aggregation in the films can be tuned by varying the volume ratio of the CB:TOL solvent mixture. In contrast to pure solvents, it is proposed that the evaporation rate difference in solvent mixtures will assist in the formation of crystal

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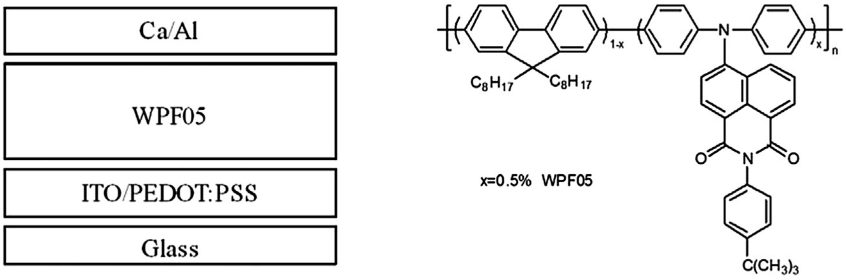

Fig. 1. Device configuration of the WPLEDs and chemical structure of single white polymer WPF05.

nucleus and enhance the crystallinity of PF backbone after annealing. The influence of the morphology of PF copolymer on the EL performance of the resulted WPLEDs is further studied. The results show that the CB:TOL solvent mixture device exhibits not only improved blue emission and thus white purity, but also more efficient light-emitting efficiency, due to the increased crystalline phase content of PF backbones that serves as efficient blue self-dopants and the more balanced charge transport. A light-emitting efficiency of 8.9 cd/A with CIE of (0.38, 0.36) is finally achieved via the CB:TOL (3:1, v/v) solvent mixture, about 134% increase compared to 3.8 cd/A of the control device processed with pure TOL solvent.

2. Experimental

The SWP used in this work is WPF05 which consists of blue fluorescent PF chemically doped with 0.5 mol% orange fluorescent 1, 8-naphthalimide moieties and its chemical structure is shown in Fig. 1 [6]. The device structure was indium tin oxide (ITO)/poly-(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (45 nm)/emissive layer (EML, 80 nm)/Ca (5 nm)/Al (150 nm). The pre-cleaned ITO glass substrates were treated with UV-ozone for 25 min. The PEDOT:PSS (Baytron P AI 4083) layer was spin-coated onto the ITO substrate and then baked at 120 °C for 45 min in air. Subsequently, the emissive layer of WPF05 was spin-coated from solutions in pure TOL or CB solvents or CB:TOL solvent mixtures with various ratios (3:1, 1:1 or 1:3, v/v), followed by annealing at 120 °C for 30 min in a glove box. The Ca/Al contacts were then thermally evaporated at a pressure of 4×10^{-4} Pa in a vacuum chamber. Topography images of the spin-cast WPF05 films were collected in air at room temperature by atomic force microscopy (AFM) using SPA300HV with an SPI3800N controller (Seiko Instruments Industry, Co. Ltd.) working in tapping mode. The bulk morphologies were investigated by transmission electron microscopy (TEM) using a JEOL JEM-1011 TEM operated at an acceleration voltage of 100 kV. A Bruker D8 Discover thin film diffractometer equipped with a copper target (Kα line) was used under a step-scan rate of 0.05° per 3 s in the scattering angle range of $2\theta = 2°-30°$ to obtain grazing incident X-ray diffraction (GIXRD) profiles of the film specimens. The current density (J)–voltage (V)–luminance (L) characteristics and EL spectra of the PLEDs were measured using a Keithley 2400 source meter and a coupled PR650 spectroscan photometer. All measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

The WPF05 films were spin-cast from TOL, CB and CB:TOL solvent mixtures with different volume ratios, respectively. The GIXRD measurement was first carried out for the WPF05 films to investigate the effect of solvent conditions on the aggregation degree of the PF backbones, and the results are shown in Fig. 2. As depicted, the detected diffraction peaks located at 6.8°, 11°, 15.8°, and 20° correspond to (200), (310), (140), and (250) + (530) reflections of the crystalline α-phase PF conformation [8]. Accordingly, the intensity of the (200) diffraction peak indeed reflects the crystalline degree of the PF backbones. It can be seen that the intensities of (200) diffraction peak are gradually increased with solvent sequence of TOL, CB, CB:TOL(3:1), CB:TOL (1:1), and CB:TOL (1:3). Thus, the crystalline degree of PF backbone chains in WPF05 films increases in the following sequence: TOL, CB, CB:TOL (3:1), CB:TOL(1:1) and CB:TOL(1:3). It indicates that the CB:TOL solvent mixtures can promote the formation of crystalline PF phase more effectively than the pure solvents, and the crystalline PF content increases with increasing the TOL ratio in the solvent mixture.

The further morphology characterization of the WPF05 films prepared from different solvent conditions was carried out by TEM measurement and the images are shown in Fig. 3. As shown in Fig. 3, the degree of nano-fibrillar aggregates in the WPF05 films gradually increase in a solvent sequence of TOL, CB, CB:TOL (3:1), CB:TOL (1:1) to CB:TOL (1:3), which is in consistent with the GIXRD results, along with the crystalline PF phase content in the films. The CB:TOL solvent mixtures promote the formation of PF backbone aggregation more effectively than the pure solvents of CB and TOL. The surface topography of the WPF05 films prepared from different solvent conditions is also investigated via AFM technology (the images are not shown here). The measured root-mean-square (RMS) roughness value is 1.70, 1.45, 3.00, 2.48 and

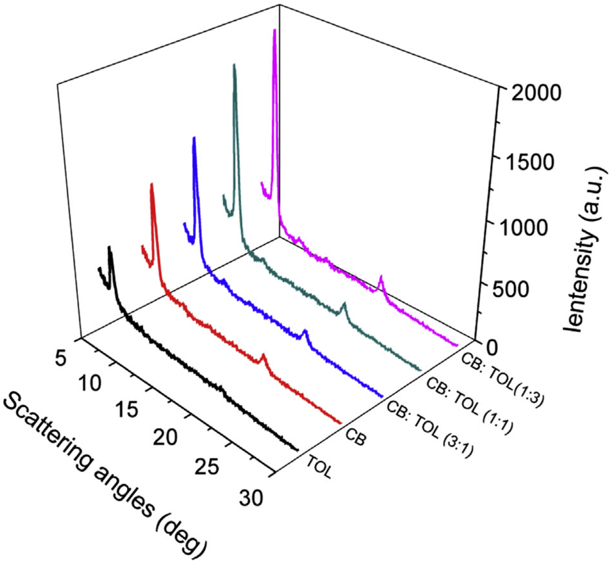

Fig. 2. GIXRD pattern of the WPF05 films spin-cast from different solvents.