SYNTHESIS AND CHARACTERIZATION OF POLYFLUORENE FLUORINATED FOR APPLICATION IN OLEDs

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ABSTRACT

We have studied the properties of polyfluorene fluorinated synthesized and the oleds properties. The alternating copolymer (poly[1,4-(2-fluoro-phenylene)-alt-9,9-dioctylfluorene]) was synthesized by Suzuki coupling reaction, here named PFP1F(P), was characterized by UV-Vis spectroscopy, Infrared spectroscopy, Thermal analysis (DSC and TGA), X-ray diffraction. The copolymer presented showed good thermal stability and crystalline moiety. The OLEDs fabricated turn on 9,0V and also was kept on for 30 min.

Keywords: polyfluorene, Suzuki reaction, fluorescence, UV-Vis Spectroscopy, organic light-emitting diode (OLED).

INTRODUCTION

Polyfluorene is a conjugated polymer that have been used as organic light-emitting diodes (OLEDs), emitting in blue region. The characteristics of this type of polymer that makes it attractive for this application are: high quantum yield of photoluminescence, good thermal stability and good solubility in common organic solvents [¹-⁴]. Polyfluorenes can be readily prepared by polymerization through Suzuki
coupling reaction, between a diboronated and a dihalogenated compound, in the presence of a catalyst based on Palladium [5,6]. In this work we have synthesized the copolymer poly[1,4-(2-fluoro-phenylene)-alt-9,9-dioctylfluorene, here named PFP1F(P), and it was characterized optical, thermal and structurally. After synthesizing the polymer, started production device with the aim of improve stability and lifetime using the materials and techniques described below[7].

EXPERIMENTAL

Materials and methods

Chemical, reagents and solvents from commercial sources are of analytical or spectroscopy grade and used as received without purification. Molecular weights were determined by Gel Permeation Chromatography using Agilent 1100 equipment with THF as solvent and polystyrene as standards. Chemical structures were attested by 1HNMR (Agilent – 400MHz) and FTIR (Thermo Scientific). Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out using TGA/DSC 1 star system and a DSC 822(Mettler Toledo), respectively. The UV-vis absorption and fluorescence spectra measurements were performed on UV-vis Spectrophotometer (Varian) and Fluorescence Spectrophotometer (Varian).

Synthesis of copolymer

A synthesis by Suzuki cross-coupling polymerization was performed under inert atmosphere[6,7]. In a two-necked flask added the monomers (1mmol), tetrakis(ytiphenylphosphine)palladium (0.012g) and some drops of Aliquat336 were dissolved in a mixture of toluene and aqueous solution of K₂CO₃ 2M. The reaction was kept under reflux at 70-75°C for 5 days, then phenylboronic acid (0.025g) was added and the reaction was ended after 2 days by cooling to room temperature. The product of the reaction was purified with hydrogen peroxide, followed by extraction with chloroform. The organic phase was finally separated and evaporated to dryness. Before precipitation in methanol, the solid residue was dissolved in CHCl₃. The purification by dissolution-precipitation was repeated at least three times until a white-yellowish solid polymer was obtained.
Device fabrication and measurements

The architecture of the device (Figure 2) was, in general, mounted in multilayer, where the base of the device was a rigid substrate (glass + ITO), on top of which layers are deposited, by spin-coating, in sequence: PEDOT:PSS (HTL - hole transport layer) / polyfluorene + butyl PBD (95/5%) / AZO - Aluminum-doped zinc oxide nanoparticle ink (ETL – electron transport layer) / Aluminum. The emitting area is determined by overlapping of two electrodes as 9 mm². The current vs voltage vs luminance relationships of devices were measured with computer-controlled Luminance & Colorimeter CS-200 (Konica Minolta) and a Keithley source measure unit.

Figure 1 - Synthetic scheme for poly[1,4-(2-fluoro-phenylene)-alt-9,9-dioctylfluorene]

Figure 2- Structure of devices with active area of 9 mm².
RESULTS AND DISCUSSION

Synthesis

The copolymer was synthesized by Suzuki polycondensation reaction of monomers in appropriate molar ratios. The reaction was performed in toluene solution with [Pd(PPh₃)₄] as catalyst and aqueous solution of K₂CO₃ 2M. The polymer was end-capped with phenyl groups. Copolymer PFP1F(p) was obtained as yellowish solid in high yield next to 95%, have good solubility in common organic solvents shuch as toluene and chloroform. The number average molecular weights (Mn) and weight average molecular weights (Mw) were determined by Gel Permeation Chromatography (GPC) as 10,550 and 23843, respectively.

Thermal properties

The thermal analyses were investigated by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) at a scanning rate of 20 ºC/min in a nitrogen atmosphere. PFP1F(p) copolymer exhibit good thermal stability with decomposition temperature over 210 ºC. When a sample was heated by DSC, a melting peak was observed at 145 ºC, wich was ascribe the crystallization, no glass transition was observed. Due to presence of peak copolymer was carried out X-ray diffraction to examine the presence of crystal phase in this sample.

Structural properties

From the X-ray diffractogram showed that copolymer have 9,0% of crystallinity, in other words, the crystal region of the sample comprises 9,0% of the total, while remaining 91% comprises the amorphous region of the copolymer.

In order to prove the existence of specific structural groups in the synthesized copolymer, we use the following techniques for evidence of chemical bonds: FTIR and ¹HNMR.

The ¹HNMR spectrum showed chemical displacement in: 7.9-7.02 (ArH), 1.2-1.0 (CH₂) and 0.9-0.7 (CH₃). Already for the infrared spectra showed high intensity band at 2926 cm⁻¹, which correspond to groups CH₂ and CH₃, at 2854 cm⁻¹ for aromatic rings and intensity in region between 1250-800 cm⁻¹ attributed for fluorinated hydrocarbons.

Photophysical properties

The photophysical properties of the copolymer were investigated by means of electronic absorption and photoluminescence spectra in dilute chloroform solutions. The figure 3 illustrates the absorption anf PL spectra. The copolymer exhibit maximum absorption peak at 365 nm. Upon photoexcitation at the absorption maximum, the polymer emit strong deep blue fluorescence, located two bands at 405 nm and 425 nm.
Based on pure blue fluorescence, good thermal stability and solubility in common organic solvents, the copolymer synthesized was used as emitting layer to fabricate Oleds with configuration substrate (glass)/ITO/PEDOT:PSS/copolymer + PBD/AZO/Al.

The current - luminance - voltage was illustrated in Figure 4. The device turned on (to deliver a brightness of 1cd/m²) at 9 V, and reached a maximum luminance of 40 cd/m² at 16V and presented CIE (2.296,0.397). In Figure 5 shows the degradation test with voltage set at 16 V up to 30 minutes.
CONCLUSIONS

The copolymer synthesized presented good reaction yield, thermal stability with certain crystallinity moiety proved by X-ray diffraction. OLEDs fabricated turn on and presented blue emission and degradation test checked the possibility to keep it on for 30 min.

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