J Mater Sci (2007) 42:4476–4479
DOI 10.1007/s10853-006-0234-1

Novel green-emitting polymer containing fluorene and 1-(2-benzothiazolyl)-3,5-diphenylpyrazoline

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Received: 6 January 2006 / Accepted: 13 April 2006 / Published online: 15 February 2007

Abstract Novel electroluminescent (EL) polymer based on fluorene having benzothiazolylpyrazoline unit in the main chain was synthesized. The result polymer possessed satisfactory thermal stability with onset decomposition temperature (T_d) of 401 °C and glass-transition temperature (T_g) of 213 °C. The polymer emits green fluorescence with high photoluminescence (PL) quantum yield of 47%. Polymer light-emitting diode (PLED) was fabricated with the configuration of ITO/PEDT 40 nm/PVK 40 nm/polymer(80 nm)/Ba(4 nm)/Al(160 nm) showed turn-on voltage of 4.5 V, and it can emit green light with maximum brightness of 1726 cd m^{-2} with the maximum external quantum efficiency of 1.59%.

Introduction

Since the discovery of polymer light-emitting diodes (PLEDs) by the Cambridge group in 1990 [1], EL conjugated polymers have attracted much interest because of their potential application in large-area flat-panel displays [2]. A large number of electroactive and photoactive conjugated polymers have been introduced during the past few years in order to obtain three primary colors for displays [3–5]. Among these polymers, PLEDs based on polyfluorene showed exceptional optoelectronic properties because they contained a rigid planar biphenyl unit and facile substitution at the remote C-9 position, which improved the solubility and processability of the polymer without significantly increasing the steric interactions in the polymer backbone [6]. As a result, polyfluorenes have emerged as very promising candidates for PLEDs due to their high fluorescence quantum yield, excellent film-forming and good thermal stability [7, 8].

Triarylpyrazoline compounds have been widely used as emitting materials in OLED [9, 10]. However, the films of small molecular pyrazolines were inferior and tend to crystallize after film formation, which lead to device degradation. The reason is that the pyrazolines monomers have low melt point [11]. In this paper, we synthesized a novel fluorene-based conjugated polymer containing benzothiazolylpyrazoline in the backbone to solve this problem.

Experimental

Materials

All the chemicals were purchased from Aldrich chemical company and were used without any further purification. All the solvents such as DMF and toluene were dried with appropriate drying agents, then distilled under reduced pressure. 1,3-bis(4-bromophenyl)-2-propylene-1-one **2** [12], 2-hydrazinylbenzothiazole [13], 9,9-dihexylfluorene-2,7-bis(trimethylene

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boronates) **4** [14] and the catalyst $Pd(PPh_3)_4$ [15] were prepared following the already published procedures.

Measurements

Microwave experiments were carried out in a modified domestic microwave oven. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 and Bruker AC-200 spectrometer. The FT-IR spectrum was obtained on a Perkin–Elmer 2000 infrared spectrometer as KBr pellets. UV-Vis spectrum of the polymer in thin film was taken on a Suhimadzu UV2100 UV-Vis recording spectrometer. Photoluminescence (PL) spectra of the polymer in solution and thin film were measured on a Hitachi 850 fluorescence spectrometer. Thermal gravimetric analysis (TGA) measurement was performed on a Perkin–Elmer series 7 thermal analysis system under N_2 at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC)measurement was performed on a Perkin–Elmer DSC 7 under N_2 at a heating rate of 10 °C min^{-1}. The weight-average molecular weight (M_w) and polydispersity indice (M_w/M_n) of the polymer were measured on a PL-GPC model 210 chromatograph at 25 °C, using THF as the eluent and standard polystyrene as the reference. The thickness of films was measured by a Dektak surface profilometer. The applied direct current bias voltage for EL device was in a forward direction (ITO, positive; Ba, negative). The current–voltage characteristics were measured on a voltmeter and an amperometer, respectively. All the measurements of the EL were carried out in air at room temperature.

Monomer syntheses

A mixture of **2** (0.56 g, 2 mmol) and 2-hydrazinylbenzothiazole (0.33 g, 2 mmol) in ethoxy-ethanol (5 mL) was placed in a three-neck flask connected with refluxing equipment. After irradiated by microwave under argon for 5 min with mechanical stirring at power output of 420 W. Then the mixture was cooled to room temperature, and the precipitate was filtered. The crude product was recrystallized from ethanol to give 1-(2-benzothiazolyl)-3,5-bis(4-bromophenyl)-4, 5-dihydro-1-H-pyrazole **3** as white powders. Yield: 87%; Mp: 208–209 °C; ^{1}HNMR ($CDCl_3$, 400 MH_Z): δ7.68–7.11 (m, 12H, Ar–H), 5.82 (m.1H, pyrazoline CH), 3.94, 3.22 (m, 2H, pyrazoline CH_2); IR (KBr pellet) 1600 cm^{-1} (S, C=N).

Polymer syntheses

The result polymer was prepared as follows: To a mixture of **3** (0.513 g, 1.0 mmol), **4** (0.502 g, 1.0 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) was added a mixture of toluene (5 mL) and aqueous 2 M potassium carbonate (5 mL). The mixture was vigorously stirred at 85–90 °C for 48 h under Ar. After the mixture was cooled down to room temperature, it was poured into 200 mL of methanol and de-ionized water (v:v, 10:1). A fibrous solid was obtained by filtration. The solid was washed with methanol, water and then methanol. After washing for 24 h in a Soxhlet apparatus with acetone, polymer **5** was obtained as a yellow powder with yield of 84% after drying under a vacuum. ^1H NMR (400 MH_Z, $CDCl_3$) δ7.89–7.10 (m, 18H, ph-H), 5.91 (m, 1H, pyrazoline CH), 4.03, 3.41(m, 2H, pyrazoline CH_2), 2.16–0.72 (m, 26H, alyl-H); ^{13}C NMR (50 MH_Z, $CDCl_3$) δ163.2, 152.5, 152.2, 151.9, 151.7, 151.6, 143.0, 141.1, 140.6, 140.4, 140.1, 139.9, 139.7, 139.4, 139.1, 138.9, 131.8, 129.9, 129.9, 128.9, 127.6, 127.3, 126.9, 126.5, 125.9, 125.6, 121.8, 121.3, 120.7, 120.1, 63.7, 63.5, 55.3, 43.7, 40.3, 31.4, 30.3, 29.6, 23.8, 22.5, 13.9. IR (KBr pellet) 1601.4 cm^{-1}(s, C=N).

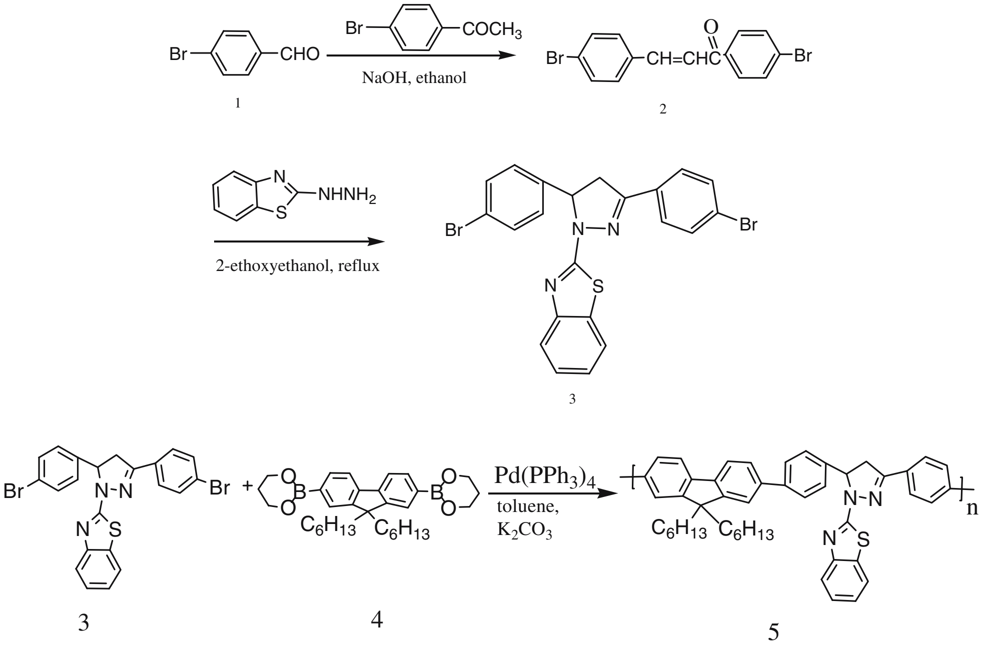
Fabrication of PLED

For the fabrication of the PLED, a thin-film made up of layers of PEDOT and PVK were spin-coated subsequently on ITO at 1500 rpm for 30 s, after which the polymer (from a 10 mg mL^{-1} polymer in toluene solution) was spin-coated on the PVK film with the same method. Finally thin layer of Ba/Al was deposited on the polymer film by thermal evaporation at a background pressure of 10^{-4} Pa. The emitting area of the device was about 6 mm^{-2}. The structure of the device is: ITO/PEDOT 40 nm/PVK 40 nm/polymer(80 nm)/Ba(4 nm)/Al(160 nm). ITO acts as anode, Ba as cathode; PEDOT and PVK acts as hole-transporting layer and the polymer is employed as the emitting layer material (Scheme 1).

Results and discussion

The polymer has weight-average molecular weights (M_w) of 28,500 with polydispersity indice 2.02. The results showed that the polymer had good solubility in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2 and toluene and could be processed into transparent thin film by spin-coating from toluene solution. As shown in Fig. 1, the polymer possesses excellent thermal stability with onset decomposition temperatures (T_d) of 401 °C, and no weight loss was observed at lower temperature. The glass transition temperature (T_g) of the polymer was 213 °C (shown in Fig. 2), which is much higher than that of typical

Scheme 1 Synthetic route of the monomer and the polymer



polyfluorene(~55 °C), indicating that the polymer can solve the crystallization problem of the pyrazoline film successfully.

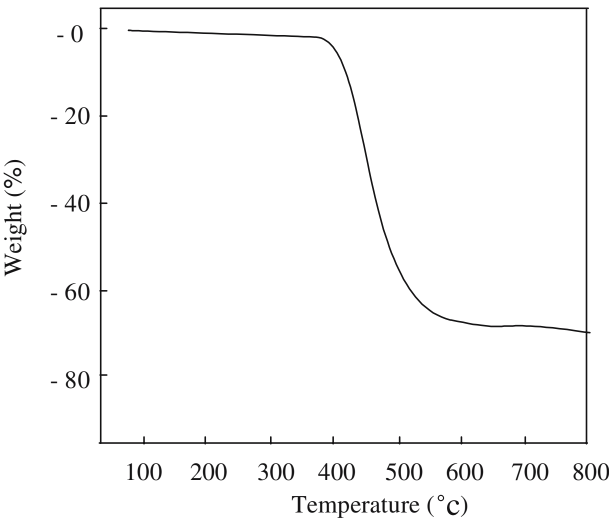


Fig. 1 TGA curve of the polymer

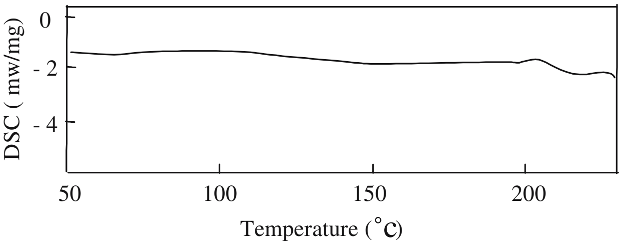


Fig. 2 DSC curve of the polymer

The absorption and emission spectra of the polymer were shown in Fig. 3. The polymer film shows very strong absorption peak at 388 nm attributed to the π–π^* electronic transitions of the conjugated polymer backbone. The optical band gap derived from the absorption edge of the thin film spectrum gave value of 2.78 eV. In the fluorescence emission spectrum of the polymer in dilute $CHCl_3$ solution at room temperature on excitation at absorption maxima, the emission peak was observed in 470 nm in the visible bluish-green region. In the thin solid film, the emission peak appeared at 501 nm in the visible green region (Fig. 3). This red-shifted effect, very common in photoluminescent polymers, is usually due to the

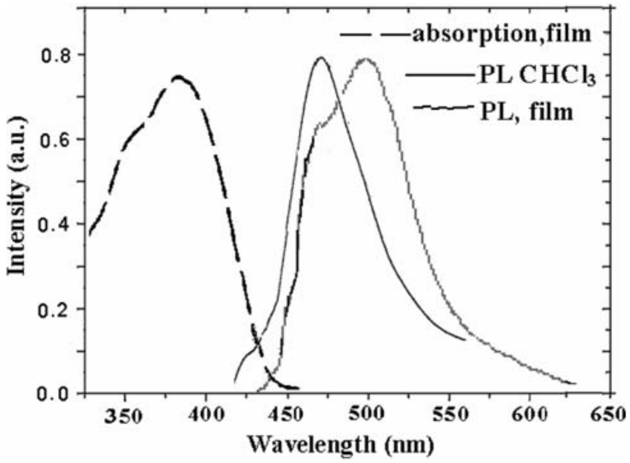


Fig. 3 UV-vis and PL spectra of polymer

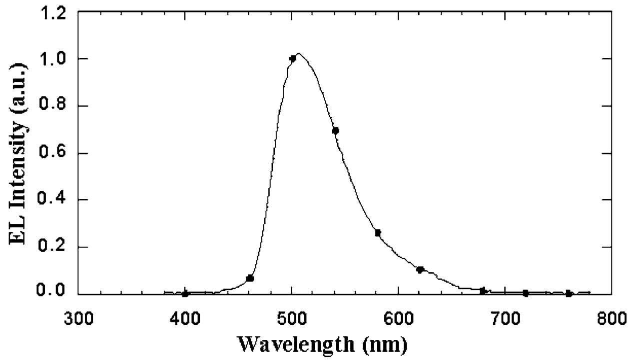


Fig. 4 EL spectrum of the PLED

stronger inter-chain interactions that could significantly reduce the energy difference between LUMO and HOMO in solid states. Full width at half-maxium (fwhm) of the film PL spectrum is 98 nm. The absolute PL quantum yield of the neat polymer film was about 47%, as measured in an integrating sphere at room temperature in air using a HeCd laser line of 405 nm as the excitation source according to the procedure described by Greenham et al. [16]. The EL spectrum of the device (Fig. 4) with maxima at 507 nm is almost identical to the corresponding PL spectrum indicating that the emission was originated from the emitting layer.

The luminance–voltage and current density–voltage characteristic of the device are shown in Figs. 5 and 6. The device emits green light starting at 4.5 V; and reaches a brightness of 1726 cd m^{-2} at a bias of 10.3 V. The maximum external quantum efficiency was measured to be 1.59% (at 7.3 V with the current density of 193 mA/cm^2 and luminance of 425 cd/m^2).

Conclusions

Novel green-emitting fluorene copolymer containing benzothiazolylpyrazoline unit in the backbone was designed and synthesized by Suzuki coupling reaction. The result polymer shows satisfactory thermal stability and excellent green emission with high PL quantum efficiency. PLED was fabricated to study its EL properties. The device shows bright green emission with high maximum external efficiency and low turn-on bias voltage. The results show that the novel polymer could act as polymer electroluminescent material.

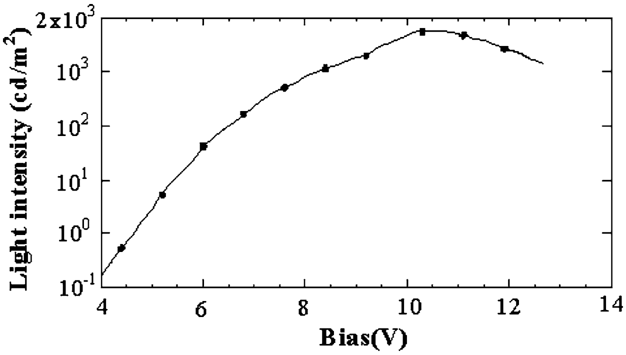


Fig. 5 Luminance–voltage curve of the PLED

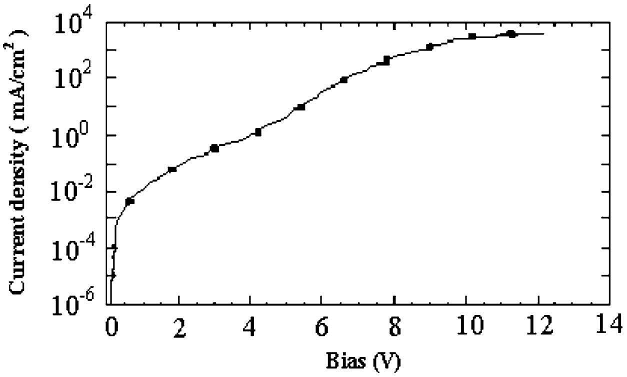


Fig. 6 Current density–voltage curve of the PLED

Acknowledgements This work was supported by the key foundation of education ministry of China (project NO. 105142).

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