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Synthesis and properties of new luminescent poly(arylenevinylene) copolymers containing spirobifluorene

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Abstract

Two new light-emitting polymers, poly[2,2'-spirobifluorylene vinylene-alt-2,5-di-(*n*-buthoxy)-1,4-phenylene vinylene] (PSBF-PV) and poly[2,2'-spirobifluorylene vinylene-alt-9,9'-di-(*n*-hexyl)-2,7-fluorenyl vinylene] (PSBF-FV) have been synthesized through the well-known Horner-Emons condensation between appropriate diphosphonates and dialdehydes. The polymers consist of arylenevinylene chromophores linked through 9,9'-spirobifuorene to control the effective conjugation length and to suppress interchain aggregation. Photoluminescence maxima of PSBF-PV and PSBF-FV in thin solid film were shown at 512 and 446nm, corresponding to green and blue-green emission, respectively. The single-layer light-emitting diodes of the two copolymers were fabricated in the configuration of ITO (indium-tin oxide)/polymer/Al, exhibiting weak emission. Better performance (luminance maxima is 846 cd/m^2) was achieved using Alq$_3$ as electron injection layer in double layer LEDs for PSBF-PV.

Keywords: Poly(phenylene vinylene) and derivatives

1. Introduction

Since PPV [poly(*p*-phenylenevinylene)] was first employed in a polymeric electroluminescence (EL) device in 1990 [1], interest in LEDs fabricated from conjugated polymers has rapidly increased. Though a wide variety of PPV derivatives have been synthesized and applied in LEDs, very few show high PL efficiencies in solid states. The major reason is that conjugated backbones tend to stack cofacially with each other due to favorable interchain interactions, which leads to a self-quenching process of excitons [2]. One effective approach to minimize these undesirable effects is to introduce proper alkyl, alkoxy [3], silyl [4], bulk rigid aryl substituents [5] and hyperbranched side groups [6]. Another approach is to introduce structural asymmetry into the polymer chain and limit its ability to pack effectively in the solid state [7].

In this paper, we describe two new partially conjugated poly(arylenevinylene)s based on 9,9'-spirobifuorene via 2,2'-linkages. Spiro-annulated molecules utilize the spiro bridge to connect two perpendicular conjugated segments via a tetrahedral bonding atom at the center [8]. The structural feature was expected to minimize the close packing of other polymer chains, thus reduce the formation of aggregates and interchain excimers, resulting in good solubility, high PL efficiency and significant increase in both phase transition temperature values and thermal stability [8,9]. In addition, the spirobifluorene moieties interrupt the conjugation via 2,2'-linkage, which provides a direct control of the conjugation length. The optical, luminescent, and electrochemical properties of two copolymers were studied here.

2. Experimental

2.1 Reagents and Materials

Compounds 1 [10], 2 [11], and 3 [12] were prepared as described in the literature. All other chemicals were used as received unless otherwise stated.

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2.2 Equipment

^{1}H NMR spectra were recorded on a Varian Unity 300MHz spectrometer using $CDCl_3$ as solvent. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) are performed using a Rigaku Thermoflex DSC8131 and TG8110, respectively, at a scan rate of 10 °C / min. UV-vis absorption spectra were recorded on a Hitachi U-3010 UV-vis recording spectrophotometer. PL and EL spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Molecular weight is determined by gel permeation chromatography (GPC) combined with static light scattering (LS) in THF solution. Cyclic voltammetry (CV) were recorded on a CHI voltammetric analyzer at room temperature in CH_3CN-containing tetrabutyl-ammonium hexafluorophosphate ($TBAPF_6$) with a scan rate of 100mV/s. We used a platinum disc as working electrode and a silver wire as quasi-referenced electrode. Ferrocene was used for potential calibration (all reported potentials are referenced against SCE).

2.3 Polymerization

The Hornor-Emmons reactions were used to obtain two polymers containing 9,9'-spirobifluorene, and the synthesis were shown in Scheme 1. General procedure was as followed [5]: A mixture of dialdehyde and an equivmolar corresponding phosphonate derivative was dissolved in anhydrous THF under an argon atmosphere. The solid tert-BuOK (2.5equiv) was added at room temperature, the mixture was heated to reflux for 36hrs. The reaction was quenched with 2% hydrochloric acid at room temperature. The polymer was precipitated from MeOH and filtered. It was purified by dissolving in $CHCl_3$ and reprecipitated from MeOH. After drying under vacuum for 24h the polymer was obtained as yellowish solid.

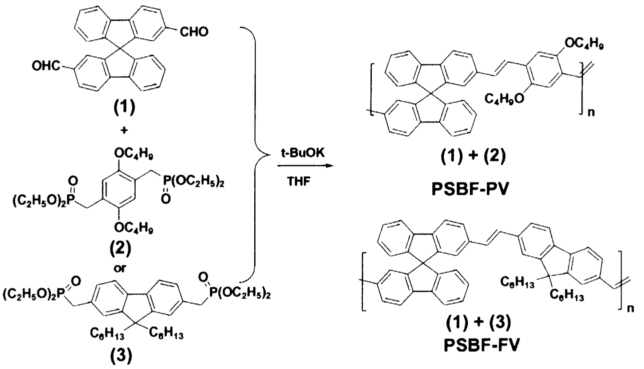
2.4 LEDs Fabrication and Measurement

EL devices were fabricated using indium-tin oxide (ITO, 30Ω/square) glass as an anode and aluminum (Al) as a cathode. The polymers were dissolved in chloroform and then spin-coated to ITO substrate. All the thermal evaporation was performed at about 4×10^{-4} Pa. The active area of devices was about 5 mm^2. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Current-voltage characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. All of the measurements were performed under ambient atmosphere at room temperature.

3. Results and Discussion

3.1 Synthesis and Characterization

An attractive way to make predominately trans-vinylene units in the polymer chain is the Hornor-Emmons condensation polymerization, as shown in Scheme 1. The polymerization of 1,4-bis(diethylphosphonate)-2,5-di-(*n*-buthoxy)-benzene, 2,7-bis(diethylphosphonate)-9,9-di-*n*-hexylfuorene with 9,9'-spirobifluorenedicarboxaldehyde to give polymers PSBF-PV and PSBF-FV was carried out in refluxing THF solution under an argon atmosphere using potassium tert-butoxide as base. The lack of aldehyde spectral signatures in ^{1}H NMR spectrum shows that no significant amount of monomeric residues remained, as showed in Fig. 1 for ^{1}H NMR of PSBF-PV. The isolated polymeric materials, PSBF-PV and PSBF-FV, were readily dissolved in THF, $CHCl_3$ and other halogenated solvents and were subjected to LS analysis to yield weight-average molecular weights (M_w's) of 21000 and 6000 with a polydispersity index of 2.19 and 1.38, respectively (Table 1). TGA revealed that PSBF-PV had high thermal stability with a 5% weight loss at 319°C. DSC thermogram of PSBF-PV showed relatively high glass transition at 204°C.



Scheme 1. Synthesis of PSBF-PV and PSBF-FV.

Table 1. Molecular weights and optical and photoluminescent data.

	M_w ($\times10^3$)	PD	Solution^a λ_{max}(nm)		Thin film λ_{max}(nm)		Φ_F^{b}
			Abs	Emi	Abs	Emi	
PSBF-PV	2.1	2.19	412	474 (505)	412	512	0.79
PSBF-FV	0.6	1.38	396	436 (464)	398	446 (469)	0.81

^{a} Spectra in chloroform. ^{b} Quantum yield was measured relative to quinine bisulfate (10^{-5}M in 1.0 N H_2SO_4).

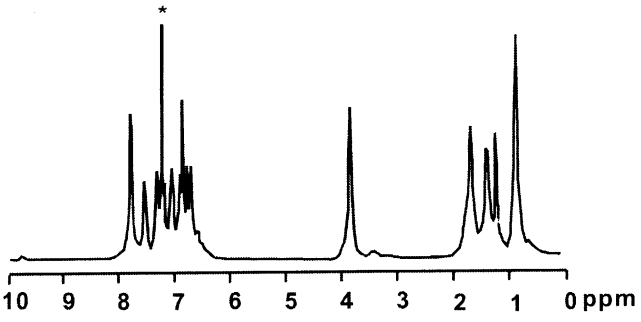


Fig. 1. ^{1}H NMR spectrum of PSBF-PV in $CDCl_3$.