Synthesis and Luminescent Properties of a New Twisted Copolymer Containing Phenylenevinylene and Spirobifluorene

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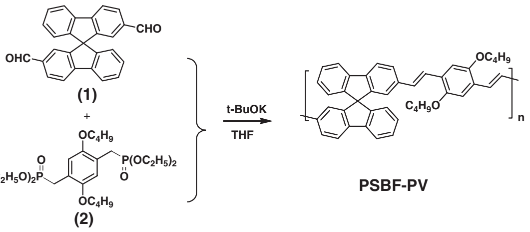
A new twisted polymer, poly[9,9′-spirobifluoren-2,2′-ylene-vinylene-alt-2,5-di(*n*-buthoxy)-1,4-phenylene-vinylene] (**PSBF-PV**), which consists of phenylenevinylene chromophores linked through 9,9′-spirobifuorene, was synthesized through the Horner–Emons condensation. **PSBF-PV** showed strong green emission in solution and film. The single-layer light-emitting diode (LED) exhibited weak emission, and an improved performance with the maximum external quantum efficiency of 0.25% and luminance maxima of 1168 cd/m^2 was achieved using Alq$_3$ as electron injection layer in double layer LED for **PSBF-PV**.

Since poly(*p*-phenylenevinylene) (PPV) 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 shows high photoluminescence (PL) efficiencies in solid states. The major reason is due to the presence of favorable interchain interactions, excimer formation, and polaron pair formation, 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 a new partially conjugated poly(phenylenevinylene) linked through 2,2′-sites of 9,9′-spirobifuorene. 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 the polymer chains, thus reduce the formation of aggregates and interchain excimers, resulting in good solubility and significant increase in thermal stability and PL efficiencies.[9] In addition, the spirobifluorene moieties interrupt the conjugation via 2,2′-linkages, which provides a direct control of the conjugation length.

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**[10] with 9,9′-spirobifluorenedicarboxaldehyde **1**[11] to give the polymer **PSBF-PV** was carried out in refluxing tetrahydrofuran (THF) solution under an argon atmosphere using potassium *tert*-butoxide as base. The isolated polymeric material was readily soluble in THF, CHCl$_3$, and other halogenated solvents.[12] No detectable amounts of *cis*-olefinic bond formation were found in ^{1}H NMR after purification. The lack of aldehyde spectral signatures in ^{1}H NMR spectrum shows that no significant amount of monomeric residues remained. Gel permeation chromatography combined with static laser scattering analysis with THF as an eluent yielded a weight-average molecular weight of 21000 with a polydispersity index of 2.19. Thermogravimetric analysis revealed that the polymer was thermally stable up to 319 °C. Differiental scanning calorimetry showed a relatively high glass transition temperature at 204 °C.



Scheme 1. Synthesis of **PSBF-PV**.

Table 1. Molecular weight and spectroscopic data

Polymer	Solution[a] λ_{max} (nm)		Thin film λ_{max} (nm)		Φ_F[b]
	Abs	Emi	Abs	Emi	
PSBF-PV	412	474 (505)	412	512	0.79

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

The photophysical properties of **PSBF-PV** were investigated in solution and solid state, as illustrated in Figure 1. The photophysical data were summarized in Table 1. Absorption spectra in dilute solution and solid state are very similar, consistent with the absence of aggregation effects in their ground electronic states. The optical band gap (E_g^{opt}) of the polymer was determined to be 2.58 eV from the film absorption spectrum edge. In chloroform, **PSBF-PV** emitted strong green fluorescence with a quantum yield of 79%. PL emission spectrum showed a red shift by 28 nm in solid state relative to dilute solution, probably due to excimer formation rather than aggregation, judging by the lack of spectral shift in the absorption spectra for the solution by comparison to the solid state.[7] The similarity of emission spectral peak maxima in PL and EL spectrum further supports the lack of substantial interchain electronic interaction.

Cyclic voltammetry was employed to investigate the redox behaviors of the polymer dip-coated on a Pt disc. In Figure 2, **PSBF-PV** showed irreversible n-doping and p-doping processes. Regarding the energy level of the SCE reference with the assumption that the energy level of SCE is 4.4 eV below vacuum,[13] the LUMO and HOMO energy levels were calculated to be

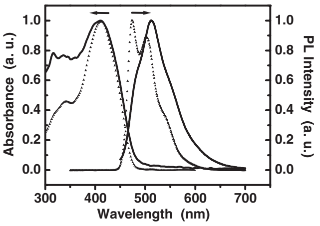


Figure 1. The optical absorption and PL spectra of **PSBF-PV** in chloroform solution (dash) and thin film (solid line).

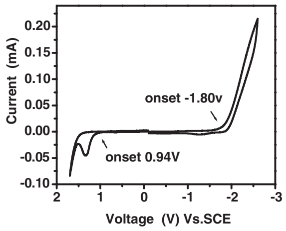


Figure 2. Cyclic voltammogram of **PSBF-PV**.

-2.60 and -5.34 eV from the onset potentials of the oxidation and reduction (E_{ox}^{onset} and E_{red}^{onset}). The high HOMO energy level suggested that the polymer exhibited good hole transport property. The electrochemical band gap (E_g^{el}) of **PSBF-PV** was estimated to be 2.74 eV according to the equation[8b] $E_g^{el} = E_{ox}^{onset} - E_{red}^{onset}$, close to that obtained by optical method.

The EL spectrum of the single-layer LED ITO (indium tin oxide)/**PSBF-PV** (60 nm)/Al (100 nm) showed a maximum peak at 516 nm with a full width about 73 nm at half-maximum, but weak emission intensity, possibly due to the imbalance of charge transport. To improve the performance, we fabricated a bilayer device ITO/**PSBF-PV** (60 nm)/Alq_3 (30 nm)/Al (100 nm). The bilayer device showed an improvement of the luminance up to 1168 cd/m^2, as illustrated in Figure 3. The maximum external quantum efficiency was measured to be 0.25% at 10.5 V with a current indensity of 38 mA/cm^2 and brightness of 244 cd/m^2. The EL maximum of the single device and the bilayer device both appeared at 516 nm, similar to the PL spectrum maximum of the polymer. However, Alq_3 was known to exhibit EL maximum about 510–530 nm, too. So the improvement behavior of the bilayer device emission was probably partially from the contribution of Alq_3. Choosing proper electron transport materials (such as TPBI or BCP) instead of Alq_3 would help to explore the emitting properties of **PSBF-PV** further.

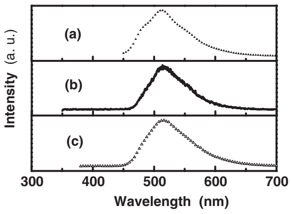


Figure 3. PL spectrum of **PSBF-PV** in thin film (a), and EL spectra of ITO/**PSBF-PV**/Al (b), and ITO/**PSBF-PV**/Alq_3/Al (c).

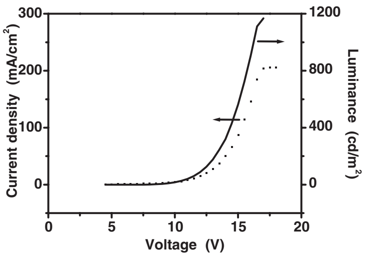


Figure 4. Current-density-brightness-voltage characteristics of ITO/**PSBF-PV**/Alq_3/Al.

In conclusion, we have synthesized a luminescent copolymer containing spirobifuorene and phenylenevinylene, in which the backbone was sufficiently twisted and the effective conjugation length was controlled. The introduction of spirobifluorene units into the PPV backbone reduced interchain interactions and improved thermal stability. The single-layer light-emitting diode was fabricated in the configuration of ITO/polymer/Al, showing weak emission. A better performance was achieved using Alq_3 as electron injection layer in the double layer LED. Optimization of the device is in progress.

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References and Notes

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12 **PSBF-PV**, FT-IR (KBr pellet, cm^{-1}): 3058 (Ar CH), 2960, 2928 (aliphatic CH), 2870 (–O–CH_2–), 1208 (Ar–O–C), 973 (*trans* HC=CH). ^{1}H NMR ($CDCl_3$): 7.8 (br m, 2H), 7.5 (br m, 2H), 7.2–7.3 (br m, 6H), 7.0 (br m, 2H), 6.9 (br m, 4H), 6.8 (br m, 2H), 6.7 (br m, 2H), 3.8 (br m, 4H), 1.25–1.69 (br m, 8H), 0.88 (br m, 6H).
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