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# RANDOM POLY(2,7-FLUORENYLENEVINYLENE) COPOLYMERS OBTAINED BY A SUZUKI-HECK REACTION: SYNTHESIS AND PROPERTIES

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## ABSTRACT

The study reports on the synthesis of poly arylene vinylenes by use of a cascade Suzuki-Heck reaction polymerization. The reaction between suitable aryl dibromides with potassium vinyltrifluoroborate in the presence of a Pd(0) catalyst permits the access to a series of poly(fluorenylenevinylene)s. The protocol is characterized by a great versatility, deriving from the use of easily attainable substrates, and yields polymers with low percentages of structural 1,1-diarylenevinylene defects. Exploiting this procedure, a series of random poly(9,9-dioctyl-2,7-fluorenylenevinylene-co-N-octyl-3,6-carbazolyenevinylene) copolymers at 20÷80% mol/mol of carbazole (**PFV2-6**) was achieved. Their properties have been investigated by <sup>1</sup>H-NMR, IR, TGA, DSC, cyclic voltammetry, UV-Vis and photoluminescence, and compared to those of poly(9,9-dioctyl-2,7-fluorenylenevinylene) (**PFV1**) obtained by the same method. The electroluminescence properties of the materials were tested by constructing OLED devices of ITO/PEDOT-PSS/**PFV1-6**/Ca/Al configuration.

## 1. INTRODUCTION

Poly(fluorenylenevinylene)s (PFVs, see scheme below) represent an attractive class of fluorescent materials and are characterized by the presence of double bonds linking two fluorenylene systems, shifting the emission of PFVs to the blue-green region with respect to polyfluorenes.

The obtainment of PFVs is commonly pursued by three major synthetic strategies: the Wittig condensation, the Heck reaction and the widely preferred Gilch route. Concerning the preparation of random fluorenylenevinylene copolymers, the properties of which have stimulated the interest of various research groups, as confirmed by a very recent work of Jin et al.[1], the Gilch approach proves very viable. In this framework, we describe a versatile method which can be applied to the obtainment of random PFVs. It consists of a reaction between a dibromo-aryl derivative with potassium vinyl-trifluoroborate, in the presence of a suitable palladium catalyst designed to promote i) a Suzuki coupling to obtain an aryl-vinyl intermediate and ii) the Heck reaction of this intermediate with another bromo-aryl system to generate the arylene-vinylene growing chain [2]. Compared to other synthetic approaches, this protocol envisages the use of aryl dibromides, that are simple and readily available building blocks for the preparation of functionalized random polyarylenevinylenes (PAVs).

This communication will focus on the synthesis and properties of new random PFVs containing variable amounts of 3,6-N-octylcarbazole in order to modulate the ionization potential and electron affinity. We investigated the possibility to modify the HOMO and LUMO energy levels of PFV segments without changing their emission properties.

## 2. MAIN RESULTS

The obtainment of **PFV1-6** (figure 1) as green powders was achieved in one-pot starting from 2,7-dibromo-9,9-dioctylfluorene and 3,6-dibromo-N-octylcarbazole in the suitable molar ratio with potassium vinyl-trifluoroborate, palladium acetate, tri(o-tolyl)phosphane and triethylamine in dioxane at reflux. Thermal analysis performed by DSC and TGA revealed good thermal stability and glass transition temperatures which depended on the copolymer composition and ranged

between 55°C and 125°C. Differently from the PL emission of the copolymers, which were found to be similar both in solution and in the solid state, their UV-Vis features evidenced a slight blue shift of the absorption maxima as function of the carbazole amount, due to the interruption of the  $\pi$ -conjugation extension caused by the 3,6-linkage at the carbazole moiety. The control of such aspect permitted the tuning of the HOMO and LUMO energy levels, that was monitored by the electrochemical properties of the materials, without remarkably changing the emission properties of the materials.

Moreover, since fluorene-based polymers are prone to fluorenone formation by C-9 oxidation, an investigation was carried out on the photoluminescence spectral stability of **PFV1** under aerobic thermal annealing. The results evidenced a remarkably higher spectral stability with respect to poly(9,9-dioctylfluorene) (POF), presumably because of the preferential oxidation of vinylene functionality with respect to the fluorene C-9 position. The absence of fluorenone formation in **PFV1** under thermal stress was confirmed by comparison with the photoluminescence features exhibited by a **PFV** containing fluorenone (10% mol/mol) as comonomer (**PFV-PFO**).

The electroluminescence properties of the polymers were tested by realizing suitable OLED devices with the configuration ITO/PEDOT-PSS/**PFV1-6**/Ca/Al. It was proven that the incorporation of carbazole in **PFV2-4** determines an improvement of the device performance with respect to **PFV1**. The best performances (450 cd/m<sup>2</sup>, 0.023 cd/A at 22 V) were obtained for the devices based on **PFV5** (60% mol/mol carbazole), due to the higher LUMO energy level (−2.99 eV) that favors the injection and transport of electrons in the device respect to the other materials. These figures of merit could be improved by inserting an electron injecting layer (Alq<sub>3</sub>) between the cathode and the polymer (890 cd/m<sup>2</sup>, 0.043 Cd/A at 10 V). These results pave the way for future studies on the optimization of HOMO-LUMO energy level of a  $\pi$ -conjugated arylene-vinylene copolymer by controlling its composition. In particular a) the Suzuki-Heck cascade method allows the obtainment of random copolymer which cannot be obtained by the classic Gilch-type approach; and b) the preparation of random copolymers can provide new opportunities for improvement of device performance by suitable choice of further electron withdrawing and electron accepting building blocks.

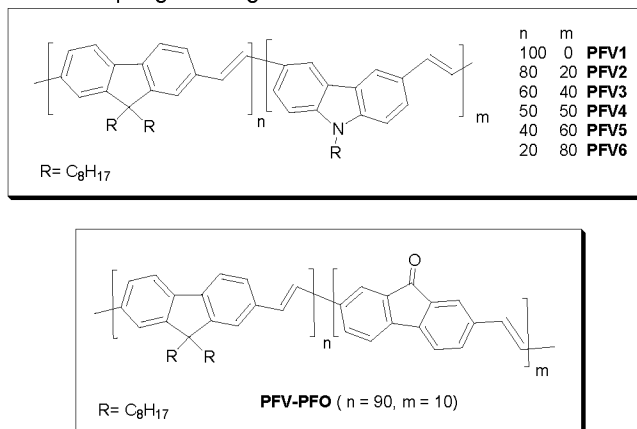


Figure 1: Poly(fluorenylene vinylenes) **PFV1-6** and **PFV-PFO**.

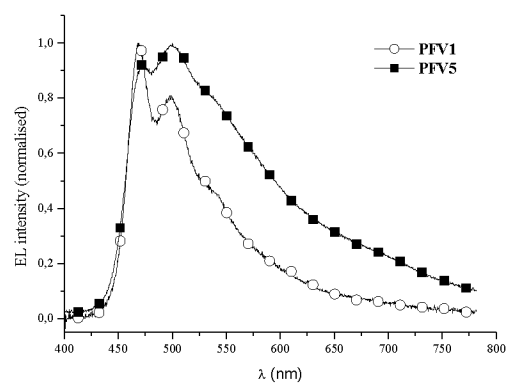


Figure 2: Electroluminescence spectra of the ITO/PEDOT-PSS/**PFV1** or **PFV5**/Ca/Al diodes at 16 V.

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