



Interplay among electronic characteristics, morphology and device efficiency in three fluorene alternated copolymers



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ARTICLE INFO

Article history:

Received 19 February 2016

Received in revised form 6 May 2016

Accepted 11 May 2016

Available online 24 May 2016

Keywords:

Fluorene

Ethylendioxythiophene

Benzothiadiazole

Photophysical properties

Conjugated polymers

ABSTRACT

Aiming to evaluate the effect of chain length on the performance of photovoltaic devices, three alternated copolymers were tested. Fluorene, chosen as a common base for comparison was linked to thiophene (Th), ethylene dioxythiophene (EDOT), and benzothiadiazole (Bz). The three comonomers were selected from the most common units in photovoltaic polymers, with different electro-affinities. The electronic properties such as frontier levels and band gap were very similar, but the chain length varied considerably, exerting a strong effect on the cell morphology. That in turn determined the charge transport efficiency and surface contact between the polymer layer and the fullerene, resulting in better performance for the polymer with the highest molecular mass, which was not the result that would be anticipated, based on the difference of electronic affinity towards to the common unit, the fluorene.

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1. Introduction

The final performance of OPV cells is governed by a series of factors that can be classified in a general way in intrinsic and extrinsic. Much effort has been devoted to enhance the intrinsic ones like judiciously choosing materials with the best values of the frontier energy levels and hence the bandgap, electroaffinity [1], charge carrier characteristics, and the important match of these properties with the frontier electronic levels of the electron carrier (fullerenes, usually). On the other hand, among the extrinsic ones, understood as those governed by processing, the morphology is the most influent parameter. In this context, the chain length, which is an intrinsic molecular factor, exerts a profound influence on morphology, an extrinsic parameter.

It is well proved that longer chains favor better morphology, the devices show higher values of roughness, increasing surface area of contact between the active polymer layer and the electron carrier [2]. The influence of morphology is widely illustrated by the improvement in device performance with thermal annealing [3,4]. This reasoning points out that this duality underlies all the efforts in achieving high performance OPVs. Therefore the comparison

among different structures would be only valid when they have the same (or near the same) molecular weight. The reverse is also true; the effect of molecular weight could only be evaluated with samples of same chemical composition. This issue was addressed in a detailed study of the systematic variation of the OPV performance with the chain length of PTB7, Mn varying from 7.5 kg mol⁻¹ to 242 kg mol⁻¹ [2,5].

In order to circumvent this issue we address the subject using three different alternating copolymers, all containing fluorene, which served as a common base for comparison. The other comonomers were thiophene (Th), ethylene dioxythiophene (EDOT) and benzothiadiazole (Bz), three of the most common units in photovoltaic polymers. As it will be shown further on, they have very similar electronic characteristics, but differ significantly in molecular weight. Fluorene was chosen due to its low lying HOMO level which is particularly interesting to reach a high open circuit voltage (V_{oc}). The perfectly alternated configuration was provided by employing the Suzuki cross coupling polycondensation reaction [6].

Concerning device configuration, there are many reports claiming the advantages of the bulk heterojunction (BHJ) structure [7,8]. Yet some recent results have demonstrated that devices with bilayer (BL) structure presenting well-defined planar interfaces may be equally or more efficient than those with BHJ architecture [9]. The polymer–fullerene BL device has several advantages over the BHJ one: the segregation of the polymer layer drastically

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reduces the exciton recombination at the donor (polymer)-acceptor (fullerene) interface and enables a better control of the individual components and interface properties during the device fabrication. Additionally, the performance of BL devices can be easily improved by the variation of the thickness of the layers to obtain a balanced transport of holes in the polymer and electrons in the fullerene. It has been demonstrated that the conduction and extraction of electrons flowing in the fullerene is the ultimate factor that limits the performance of organic solar cells in both BL and BHJ architectures [3,10]. On top of that, differences in phase configurations of the polymer-fullerene blends due to solubility and interaction parameters would be eliminated, when comparing the OPV behavior of the three copolymers [11].

A detailed study of the opto-electronic characteristics was undertaken in order to provide a basis for comparison and thus infer the interplay among those and the final morphology, which is mostly dependent on molecular weight.

2. Experimental

2.1. Materials and characterization

All chemicals were purchased from either Sigma Aldrich or Acros and used without further purification, otherwise noted. The solvents methanol, toluene, tetrahydrofuran (THF) and acetone were used as received, chloroform was treated as indicated in the literature before using [12].

^1H NMR spectra were recorded in deuterated chloroform on a Brücker equipment at 400 MHz, chemical shifts were recorded in parts per million (ppm), and splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). The molecular weights of all copolymers were determined by an Agilent 1100 gel permeation chromatograph (GPC), connected with UV and RI detectors using tetrahydrofuran (THF) as an eluent, analyzer with two columns, concentration: 2 g L^{-1} in THF, the calibration curve was built with polystyrene standards, at a flow rate of 1.0 mL min^{-1} , at 25°C .

UV absorption spectra were recorded on a Shimadzu spectrophotometer model NIR 3101. Steady-state fluorescence spectroscopy was performed in Shimadzu spectrophotometer model RF5301-PC, using a square cuvette of 1 cm. The spectral range was 250–550 nm for the excitation spectra and from 450 to 600 nm for emission spectra. Slits were selected for a spectral resolution of $\pm 1\text{ nm}$ in excitation and in emission. Solid state absorption and fluorescence spectra were obtained on thin films coated on a quartz substrate prepared from polymer solution in chloroform.

Cyclic Voltammetry (CV) was performed on a potentiostat galvanostat PAR 273A at a room temperature and a scan rate of 50 mV s^{-1} . A conventional three-electrode system in a three necked cell with a lid cover consisting of a platinum electrode tip (3 mm diameter), a platinum wire, and a Ag/AgCl electrode was used as working, counter, and reference electrodes, respectively. The working electrode was composed by cast films of the copolymers onto FTO covered glass slides. The solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile was used as the supporting electrolyte.

Thermal decomposition temperatures of the polymers were determined by a Netzsch Thermisch Analyser TG 209. For the thermogravimetric tests (TGA) a heating rate of $20^\circ\text{C min}^{-1}$ was used with a nitrogen flow of 15 mL min^{-1} from room temperature to 600°C . The DSC equipment used was a Netzsch DSC 204 F1. All the samples were heated from 20 to 350°C at a rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere and then cooled down to 20°C at $10^\circ\text{C min}^{-1}$. This procedure was repeated and the second run was recorded.

The polymer films thicknesses were determined in a Dektak 3 profilometer. Topography images were acquired by using an

atomic force microscope (AFM, Shimadzu SPM 9500J3) in dynamic mode. The photovoltaic characterization was performed with a Keithley picoammeter with power supply, model 6487. The solar simulation was made using air mass (AM1.5) filter with a power illumination of 100 mW cm^{-2} from a 150 W Oriel Xenon lamp.

2.2. Polymer syntheses

General synthesis procedures of the copolymers through the Suzuki coupling reaction are described as follows:

Poly[(9,9'-*n*-dihexyl-2,7-fluorene)-alt-2,5-thiophene] – P(FTh): To a mixture of 2,5-thiophenediboronic acid (0.366 g, 2.13 mmol), 2,7-dibromo-9,9'-*n*-dihexylfluorene (1.0 g, 2.03 mmol), and tetrakis (triphenylphosphine) palladium(0) (1.0 mol%) was added a degassed mixture of toluene (30 mL) and 2 M aqueous potassium carbonate (10 mL, 20 mmol). The mixture was vigorously stirred at 90°C during 5 days under the protection of argon. Degassed 2-bromobenzene (1.0 mol%) in toluene solution (5% of the total volume), was then added and vigorously stirred at 90°C during 12 h. The reaction mixture was cooled to room temperature and slowly added to a vigorously stirred mixture of methanol/acetone/HCl (1 M). The precipitate was collected by filtration. The polymer was purified by chromatography (silica gel, CHCl_3) and by Soxhlet extraction in methanol, resulting 0.60 g of the yellow solid (yield 72.4 %). ^1H NMR (400 MHz, CDCl_3 , ppm): 0.71 (brm, 10H aliphatic), 1.07 (brm, 12H aliphatic), 2.03 (brm, 4H aliphatic), 7.67–7.30 (brm, 8H aromatic). Elemental Analysis – Calcd. for $\text{C}_{29}\text{H}_{34}\text{S}$ (%): C, 84.05; H, 8.21; S, 7.73. Found: C, 84.05; H, 8.42; S, 7.62.

Poly[(9,9'-*n*-dihexyl-2,7-fluorene)-alt-2,5-(3,4-ethylenedioxythiophene)] – P(FEDOT): To a mixture of 9,9'-dihexylfluorene-2,7-diboronic acid (0.572 g; 1.35 mmol), 2,5-dibromo-3,4-ethylenedioxythiophene (0.406 g; 1.35 mmol), tetrakis(triphenylphosphine) palladium(0) (1.0 mol%) and potassium carbonate (2.146 g; 20.2 mmol) was added toluene (30 mL) and a mixture of water (15 mL) containing 0.25 mL of aliquat. The mixture was kept under reflux with vigorous stirring for 72 h under a nitrogen atmosphere. The end groups were capped by reacting with bromobenzene under reflux for 12 h in an argon ambient (1.1 equiv. with respect to diboronic acid monomer). After end capping, the mixture was cooled and precipitated by pouring the mixture onto an excess of methanol. The polymer was re-precipitated with CHCl_3 /methanol. Impurities and oligomers were eliminated by Soxhlet extraction. After concentration, the product was obtained as 0.51 g of a green solid (yield 81%). ^1H NMR (CDCl_3 , 400 MHz, δ ppm): 0.76-(m, 10H aliphatic), 1.03–1.2 (m, 12 aliphatic), 1.94–2.1 (m, 4H aliphatic), 4.45 (s, 4H aliphatic), 7.69 (m, 4 aromatic), 7.82 (d, $J=8.1\text{ Hz}$, 2H aromatic). Elemental Analysis – Calcd for $\text{C}_{31}\text{H}_{36}\text{S}$ (%): C, 78.81; H, 7.63; S, 6.78. Found: C, 78.11; H, 7.64; S, 6.25.

Poly[(9,9'-*n*-dihexyl-2,7-fluorene)-alt-(2,3,5-benzothiadiazole)]-P(FBz): To a mixture of 9,9'-dihexylfluorene-2,7-diboronic acid (0.50 g; 1.84 mmol), 4,7-dibromobenzo[1,2,5]thiadiazole (0.348 g; 1.84 mmol) tetrakis (triphenylphosphine) palladium (0) (1.0 mol%) and potassium carbonate (2.542 g; 18.4 mmol) was added toluene (40 mL) and a mixture of water (15 mL) containing 0.25 mL of aliquat. The mixture was kept under reflux with vigorous stirring for 72 h under an argon atmosphere. The end groups were capped by reacting with bromobenzene under reflux for 12 h in an argon ambient (1.1 equiv. with respect to diboronic acid monomer). After end capping, the mixture was cooled and precipitated by pouring the mixture onto an excess of methanol. The polymer was re-precipitated with CHCl_3 /methanol. Then the polymer was purified following the procedures described above. The product of this polymerization was 0.66 g of a green solid, yield was 78%. ^1H NMR (CDCl_3 , 400 MHz, δ ppm): 0.75–1.06 (m, 10H aliphatic), 1.11–1.26 (m, 12H aliphatic), 2.02–2.31 (m, 4H aliphatic), 7.63–8.18 (m, 8H

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