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Design, Synthesis, Characterization and Use of Random Conjugated Copolymers for Optoelectronic Applications

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Abstract. We report the synthesis and the optoelectronic characterization of a new family of random conjugated copolymers based on 9,9-bisalkylfluorene, thiophene and benzothiadiazole monomers unit synthesized by a palladium-catalyzed Suzuki cross-coupling reaction. The photophysical, thermal, electrochemical properties were investigated. The electronic structures of the copolymers were simulated via quantum chemical calculations. Bulk heterojunction solar cells based on these copolymers blended with fullerene, exhibited power conversion efficiency as high as 1% under illumination of 97 mWcm⁻². One of the synthesized copolymers has been successfully tested as active layer in simple light-emitting diode, working in the green spectral region and exhibiting promising optical and electrical properties. This study suggests that these random copolymers are versatile and are promising in a wide range of optoelectronic devices.

Keywords: conjugated polymer, random, organic solar cell, organic light-emitting diode.

1 Introduction

The field of organic optoelectronics is growing up since the late 1980s [1]. The research has been largely driven by design and development of different types of functional materials for optoelectronic applications such as organic light-emitting diodes (OLEDs) [2], organic solar cells (OSCs) [3], organic field-effect transistors (OFETs) [4], etc. The common feature of these applications consists of using materials with suitable transport and optical properties. Conjugated polymers are a class of materials that are gaining great attention by the scientific community due to its potential of providing environmentally safe, flexible, lightweight and inexpensive electronics. They show flexibility in synthesis, high yield of charge generation when mixed with electron acceptor materials and good stability. Furthermore, they have relatively high absorption coefficients [5] leading to high optical densities in thin solid films. Among the conjugated polymers, alternating fluorene copolymers (APFO) [6] and their derivatives have been widely used for efficient organic devices. In particular, the APFO-3 polymer has demonstrated efficiencies as high as 4.2%. In this polymer the fluorene unit has been used in conjunction with alternating electron-withdrawing (A) and electron-donating (D) groups. The structure is a strictly *alternating* sequence of fluorene and donor-acceptor-donor (DAD) units. Conjugated *random* copolymers are, by far, less used than alternating copolymers for devices fabrication. While the disordered structure may hamper the crystallization and decrease the carrier mobility, the presence of different monomer units sequences generate a distribution of energy gaps and increase the light harvesting ability. Furthermore an advantage of random copolymers lies in their simplicity of synthesis that consists in a one-pot polymerization step from readily available precursors. In this work we report the synthesis and characterization of a novel family of conjugated copolymers based on same the monomeric units of APFO-3 (F: fluorene, T: thiophene, B: benzothiadiazole) but having a pseudorandom structure. We applied these new copolymers in solar cells and bright green OLEDs.

2 Technological Innovation for Sustainability

The development of sustainable energy production is a topic of growing importance in view of the limited supply of fossil fuels, which is expensive financially and not environmentally friendly. One of the possible sustainable energy sources is the sun, which makes the development of photovoltaic devices interesting. Currently, the market of photovoltaic is dominated by silicon cells technology. However, it is still not cheap enough to allow a wide diffusion in the absence of government incentives. For this reason huge efforts of research and development have been spent to find alternative and improved solutions. Organic devices are lightweight and can be made flexible, opening the possibility for a wide range of applications. Our contribution in this field is the development of promising organic materials for photovoltaic and optoelectronic applications. In particular, our work revolves around the conjugated

polymers that have received considerable attention because of their promising performance. In this paper we report the synthesis and characterization of a family of novel conjugated copolymers having a pseudorandom structure. The synthesis of random instead of alternating copolymers has the aim to improve the harvesting of the sunlight. Indeed, the mixture of possible copolymer resulting from the statistical combination (in condition of equal affinity between the monomers that form copolymers) results in a broadening of the absorption bands due to overlapping of different energy levels. This is one of fundamental prerequisites in order to obtain high efficiency photovoltaic devices.

3 Experimental

Three different pseudo-random copolymers (**PFB-co-FT**, **PBT-co-BF**, **PTF-co-TB**) were synthesized by a palladium-catalyzed Suzuki cross-coupling reaction [7] from dibromides and boronic diacids or diesters. More details can be found elsewhere [8]. The weight-average molecular weight (M_w) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using THF as eluent and monodisperse polystyrenes as internal standards. UV-Visible absorption spectra of all copolymers was recorded at room temperature with a Lambda 950 spectrophotometer. Electrochemical measurements were performed with an Autolab PGSTAT30 potentiostat/galvanostat in a one compartment three-electrode cell working in argon-purged acetonitrile solution with 0.1 M Bu_4NBF_4 as supporting electrolyte. We used a Pt counter electrode, an aqueous saturated calomel (SCE) reference electrode and a Glassy Carbon working electrode which was calibrated against the Fc^+/Fc (ferricenium/ferrocene) redox couple, according to IUPAC [9]. The films formed on the electrode were analyzed at a scan rate of 200 mV/s. OSCs were fabricated by first spin-coating poly(ethylenedioxythiophene:polystyrenesulfonic acid) (PEDOT:PSS) on top of cleaned, pre-patterned indium-tin-oxide (ITO) coated glass substrates as polymer anode (50 nm in thick). The anode polymer film was then annealed at 120°C for 10 min. The copolymers blended with PCBM in solution were deposited on the top of PEDOT:PSS by spin-coating. The cathode consisting of Al (70 nm) was then sequentially deposited on top of the active layer by thermal evaporation in vacuum lower than 10^{-6} Torr giving a sandwich solar cell structure of ITO/PEDOT:PSS/Copolymer:PCBM/Al. Current density-voltage characteristics were measured using a Solar Simulator Abet 2000 (Class A, AM1.5G). All characterization was carried out in an ambient environment. OLEDs were fabricated by the same procedure as that of solar cells but in this case the only copolymer in solution were deposited on the top of PEDOT:PSS by spin-coating. The corresponding configuration of devices was ITO/PEDOT:PSS/Copolymer/Al. Steady-state Photoluminescence (PL) spectra were recorded at room temperature with an Fluorolog 3 spectrofluorometer. The steady state current-voltage (I-V) characteristic was recorded by NI-USB 6229 National Instruments acquisition card. The electroluminescence (EL) spectra were collected installing the device inside the sample chamber of an IF 650 (Pelkin Elmer) spectrophotometer, working in emission

mode, by injecting a current of 1 mA. To this purpose a HP E3631 triple output power supply was used as a constant current generator.

4 Modeling

In order to understand the correlations between property and structure, theoretical calculations were carried out. The calculations of HOMO/LUMO distribution of copolymers were performed in two steps. The monomeric units were first modeled by using a quantum mechanical Hartree Fock methods [10]. In the second step we obtained the geometric optimization of monomers and oligomers by a density functional theory approach [11]. The performed calculations showed how HOMO and LUMO positions are affected by electron-donating and electron-withdrawing groups. The last occupied orbital is localized primarily on the electron-rich units of the molecule (Fluorene and Thiophene) while the first empty orbital is essentially localized on the electron-poor unit (Benzothiadiazole). This means that the molecular orbitals are not extended to the whole structure, but are confined in a limited region of space. This has important implications both in the exciton formation and in the charge transfer. Following the model results we can conclude that the charge *hopping* among localized sites is one of the main transport mechanism. In order to obtain an electronic transfer between the copolymer and the PCBM, the latter should be close to a benzothiadiazole unit. On the other hand, the fact that a partial charge separation already exists, may promote the formation of excitons and extend their lifetime.

5 Results and discussion

Material synthesis: The chemical structures of all synthesized copolymers is showed in Fig. 1. In the three copolymers, in turn, each F, T, B comonomer unit is alternated to the other two units, which are randomly distributed. The weight-average molecular weight (Mw), and polydispersity indices (PDIs) are summarized in Table 1.

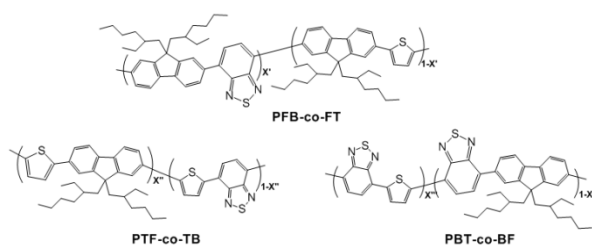


Fig. 1. Chemical structure of the synthesized copolymers.

The properties of conjugated polymers are remarkably sensitive to the presence of impurities, which might act as uncontrolled dopants, traps of charge carriers,

quenchers of excited states, etc. To improve the performance the copolymers solution was treated by ammonia and ethylenediaminetetraacetic acid to remove contaminants such as catalyst residue and side-products from copolymers synthesis. (See Table 2). *Optical properties:* Absorption spectroscopy provides information about the spectral coverage and the magnitude of the optical energy gap that are an important parameters in device designing. The UV-Vis absorption spectra of the copolymers in thin films are shown in Fig. 2.

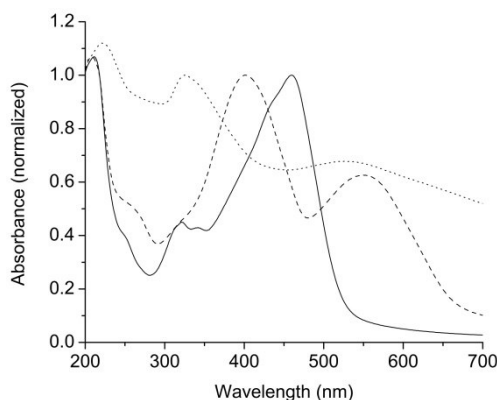


Fig. 2. Absorption spectra of films of random copolymers **PFB-co-FT** (solid curve), **PTF-co-TB** (dash curve) and **PBT-co-BF** (dot curve), normalized at the band around 400 nm.

The optical energy gap of the copolymers was estimated from the onset of absorption and data are reported in Table 1.

Electrochemical properties: Cyclic voltammetry (CV) was employed to estimate the HOMO and LUMO energy levels of copolymers. Electrochemical data were calculated from the onsets of oxidation and reduction potentials [12]. The data obtained are reported in Table 1 and schematized in Fig. 3.

Table 1. Molecular weights, optical and electrochemical data of copolymers

Entry	GPC		UV-Vis absorption		Cyclic Voltammetry		
	M_w (g/mol)	PDI	E_g^{opt} (eV)	λ_{max} (nm)	$E_{on}^{ox}/HOMO$ (V)/(eV)	$E_{on}^{red}/LUMO$ (V)/(eV)	E_g^{cv} (eV)
PFB-co-FT	34600	3.00	2.38	321/460	0.81/-5.61	-1.93/-2.87	2.74
PTF-co-TB	3200	1.80	1.86	402/552	0.51/-5.31	-1.54/-3.26	2.05
PBT-co-BF	1600	2.60	1.40	326/526	0.21/-5.01	-1.40/-3.40	1.61

The electrochemical gap is greater than the optical gap calculated from the UV-Vis spectra. This discrepancy is usually related to the charge carriers formation in voltammetric measurements [13]. All the copolymers have HOMO and LUMO levels higher than the commonly used [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM)

acceptor [14] (see Fig 3). **PFB-co-FT** exhibits the higher molecular weight and the higher energy gap compared to the other two copolymers. Furthermore is the copolymer with the highest $E_{\text{HOMOdonor}}-E_{\text{LUMOacceptor}}$ difference. On this basis **PFB-co-FT** is expected to lead to photovoltaic devices with the better V_{oc} [15]. The $E_{\text{HOMOdonor}}-E_{\text{LUMOacceptor}}$ difference of **PTF-co-TB** is lower, but the smaller energy gap could compensate the expected lower V_{oc} with a higher J_{sc} in designing an efficient solar cell. **PBT-co-BF**, is the copolymer with the lower energy gap and this would makes it the best candidate for OSCs.

Table 2. Elemental analysis of copolymers at different stages of purification.

Entry	Before purification		After purification	
	Pd (ppm)	P (ppm)	Pd (ppm)	P (ppm)
PFB-co-FT	3400	800	10	700
PTF-co-TB	1100	800	100	800
PBT-co-BF	30000	9000	5000	900

5.1 Conjugated Polymer-Based photovoltaic devices

Photovoltaic devices were fabricated in a typical sandwich structure of glass-ITO/PEDOT:PSS/Copolymer:PCBM/Al, using copolymers as electron donors and the PCBM as electron acceptor. Photovoltaic characterization includes different approaches to optimize the efficiency of the devices. The parameters taken into account were: selection of the best solvent, optimization of D:A weight ratio, optimization of the active layer thickness and analyzing annealing effects. We have investigated the effects of three different solvents on the photovoltaic performance: Chloroform (CF), Chlorobenzene (CB) and orto-DiChloroBenzene (o-DCB), individually and in a mixture form. The copolymer **PBT-co-BF** showed very low solubility and the tendency to agglomerate in all solvents; this made difficult to obtain a good film and accordingly devices. In order to choose the best blend composition, active layers with D:A w/w ratios 1:1, 1:2, 1:3, and 1:4 were studied. The photovoltaic parameters of the best cells are summarized in Table 3.

Table 3. Photovoltaic parameters of the best solar cells. The active area was 0.22cm^2 .

Donor	Acceptor	D/A ratio (w/w)	Solvent	C (mg/ml)	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	η (%)
PFB-co-FT	PCBM	1:2	CB:CF (1:1 v/v)	10	0.92	0.90	0.40	0.35
PTF-co-TB	PCBM	1:4	CB	5	0.94	3.43	0.31	1.08

Fig. 3 shows the J-V curve of the best devices in the dark and under AM 1.5G simulated sunlight at an intensity of 97mWcm^{-2} . The active layer thickness was 100 nm for all cells. The effects of thermal annealing were also studied but it has shown a negative effect in all cases.

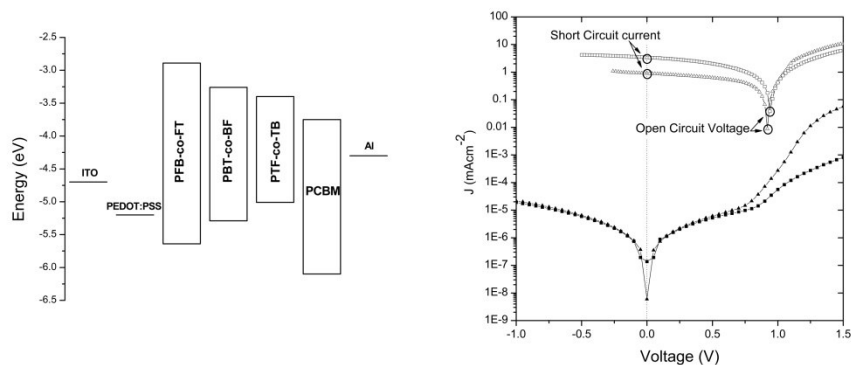


Fig. 3. Energy level diagram of the device components (*Left*); J-V curve of the best solar cells for **PFB-co-FT** (*triangle*) and **PTF-co-TB** (*square*) in the dark (*black*) and under illumination (*white*) (*Right*).

5.2 Light-emitting diode based on Conjugated Polymer

Among all copolymers investigated, **PFB-co-FT** has been recognized as promising material for green emitters due to its photoluminescence efficiency. The normalized UV-Vis and PL spectra of copolymer are shown in Fig. 4; the absorption maxima is at 460 nm while the emission maxima is at 543 nm. The devices was fabricated in a simple structure of glass/ITO/PEDOT:PSS/Copolymer/Al. The EL spectra of the device, is showed in Fig. 4.

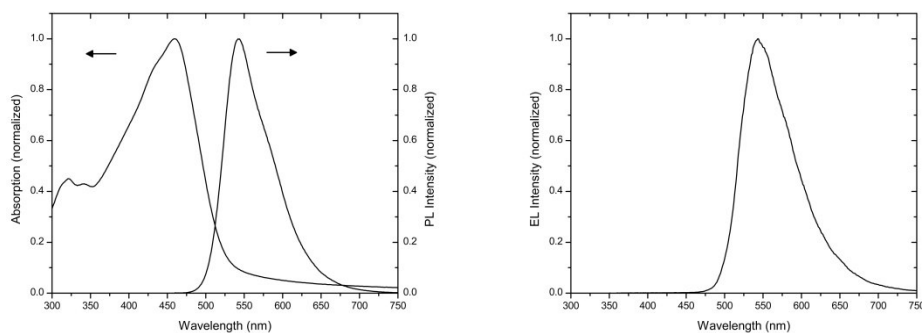


Fig. 4. Normalized UV-Vis absorption and PL spectra for the **PFB-co-FT** copolymer in film (*Left*); Normalized EL spectra of the device recorded at 7.65 V and 1mA (*Right*).

After one month of storage at room temperature the device was re-examined, with identical results and without degradation. This outcome confirms the good stability of the film.

Conclusions

In this work we have synthesized a novel family of random copolymers. The optical and electrochemical behaviors of the materials were measured and the optoelectronic performance were tested. The results clearly demonstrated that there is a correlation between the chemical structure and the HOMO levels determined from electrochemical studies as well as the V_{oc} values determined from photovoltaic devices. **PTF-co-TB** showed interesting photovoltaic properties with V_{oc} of 0.94 V and an efficiency over 1%. The **PFB-co-FT** copolymer was tested as active layer in a simple OLED. The device emits in the green and might be a promising candidate for electroluminescent materials due to its excellent luminescent properties, solubility, film-forming property and stability. We can conclude that this class of copolymer materials is very promising for optoelectronic applications.

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