



New copolymers with fluorinated and non-fluorinated benzothiadiazole units for efficient single layer near infra-red photodiodes with fast time response

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ABSTRACT

We describe the synthesis and photodetecting properties of new, low band-gap copolymers: P1 with 5,6-difluoro-2,1,3-benzothiadiazole and P2 with 2,1,3-benzothiadiazole, both containing diketopyrrolopyrrole acceptor units. These compounds have been used for fabrication of single layer, solution processed photodetectors. For this purpose, two blends with fullerene derivative (6,6)-phenyl-C61-butyrac acid methyl ester ([60]PCBM): P1: [60]PCBM and P2:[60]PCBM, were prepared and applied as active layers in bulk-heterojunction photodiodes. For near infrared light (810 nm), these photodetectors, in spite of single layer structure, display competitive performance, showing specific detectivity up to $5 \cdot 10^{11}$ Jones, responsivity up to 0.3 A/W and rise and fall times of the transient signals below 10 μ s.

1. Introduction

Organic electronics based on soluble polymer semiconductors offers a possibility of producing electronic devices by means of simple and cheap techniques, e.g. printing, which are not accessible for conventional silicon electronics. Coupled with other unique properties of “plastic” electronic devices, such as flexibility, conformability or low weight, this emerging technology opens new fields of applications, including wearable electronics, and thin-film biosensors for medical devices, textiles, toys, etc. Since the discovery of organic solar cells based on conjugated polymer/fullerene bulk heterojunctions more than a decade ago, the efficiency of these devices has been steadily increasing. The progress has been made possible mainly due to the development of new conjugated electron-donor copolymers [1] and the appropriate acceptor materials [2,3]. The “push – pull” concept, which is widely utilised in the design of novel materials, is based on combining different electron-rich and electron-deficient heterocycles in an alternating copolymer chain. The optoelectronic properties of push-pull copolymers can be precisely controlled by selecting the appropriate electron donor

and acceptor blocks. In particular, it was possible to optimise the values of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the polymers, as well as their band gaps to match the electronic characteristics of the acceptor counterparts. The (6,6)-phenyl-C61-butyrac acid methyl ester ([60]PCBM), and similar C_{70} derivatives, have been the most widely used acceptor materials in polymer organic photodiodes for almost two decades [4].

In photodetectors, either photoresistors or photodiodes, incoming light controls the flow of electric current. As such, photodetection should be characterised by low electrical current in the dark, a rapid, considerable increase of the current upon illumination, and a fast decrease of the current when the light is off [5]. Photoresistors can exceed the external quantum efficiency (EQE) of photodetectors and are preferred when the highest possible responsivity is required. The advantage of photodiodes over photoresistors results from faster response and, moreover, they can work in the photovoltaic mode and detect light without applied bias voltage. The organic semiconductors are particularly attractive for large area semi-transparent photodetectors because

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of the possibility of tuning their optical characteristics and action spectra. Furthermore, organic electronic devices can be produced with relatively simple techniques (e.g. by printing and roll-to-roll techniques) allowing for low cost per unit area.

The principle of operation of the organic photodiode is based on light induced creation of the excitons (electron-hole pairs) and their separation under the electric field. The electric field is induced by the sum of the built-in potential (difference in the electrode work functions), and the externally applied bias voltage. The free electrons and holes created by the dissociation of the excitons are transported through the active layer and collected at the respective electrodes. The main figures of merit characterising the photodiode performance are the specific detectivity, the responsivity, and the response time [6]. The reported polymer-based photodetectors typically show specific detectivity in the range 10^{10} to 10^{13} Jones [7,8], and the responsivity ranging from 0.2 to 5 A/W [9,10], depending on the wavelength; in general, the near-infrared photodetectors exhibit lower responsivity and specific detectivity than the visible light photodetectors [11,12]. The response time is defined as the rise and fall times of the transient photocurrent and these are below 20 μ s for the reported optimised polymer photodetectors [10].

In this work, we present two new low band-gap co-polymers. The polymers P1 and P2 primarily differ by fluorination of the benzotriazole group in P1. The better performance of devices with fluorinated copolymer compared to devices with their non-fluorinated counterparts can be attributed to several mechanisms. In literature the “fluorine effect” is connected with the electron-withdrawing nature of the fluorine substituents, and additionally fluorinated copolymers exhibit tendency for self organisation what results in an improvement in charge carriers mobility and in suppressing of the losses connected with recombination [13]. There are several reports describing solar cells based on fluorinated polymer which demonstrate higher open circuit voltages and short-circuit current densities, resulting in higher power conversion efficiencies, as compared with their non-fluorinated analogues [14–16].

We used both materials in photodiodes which had been tested in photovoltaic and photodetector modes. We describe both the synthesis and the detailed results of photodiode characterisation. In our studies we have used devices of simple structure, in which all active layers, with the exception of the electrodes, were deposited from the solutions. The motivation for such an approach was to fabricate the photodiode structure which in near future could be manufactured by means of printing techniques such as ink-jet printing or screen printing [17].

2. Experimental

2.1. Synthesis of conjugated polymer P1

The monomers **M1** [18] (0.5 g, 0.42 mmol) and **M2** [15] (0.57 g, 0.42 mmol) (Fig.1) were introduced into a 50 mL round-bottom three-necked flask equipped with a reversed condenser and thermometer. Anhydrous toluene (30 mL) and tetrakis(triphenylphosphine)palladium (0) (10 mg) were added. The reaction mixture was deaerated, immersed in an oil bath and heated at reflux for 6–7 hours. The molecular weight characteristics of the formed polymer were monitored every 30 min. The reaction was terminated when the weight average molecular weight M_w neared 200 kDa. Then the reaction mixture was cooled down to room temperature, and polymer was precipitated by addition of 150 mL of methanol. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, acetone, chloroform, and chlorobenzene. Subsequently, the chlorobenzene fraction was concentrated to ~20 mL and the final polymer was obtained by precipitating into methanol followed by drying in vacuum. The total yield of the purified polymer **P1** was 72%. $M_w = 233$ kDa, $M_w/M_n = 1.5$.

2.2. Synthesis of conjugated polymer P2

The key monomer **M3** was obtained in the Stille cross-coupling reaction between **M1** and 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole prepared as described previously [10]. Briefly, **M1** (0.5 g, 0.42 mmol) and 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.25 g, 0.84 mmol) were placed in a three-neck round-bottom flask and added were 30 mL of toluene and 10 mg (0.0086 mmol) of tetrakis(triphenylphosphine)palladium(0). The obtained reaction mixture was deaerated and then stirred vigorously at reflux for 24 h. After completion of the reaction, the mixture was cooled down to room temperature and poured into 150 mL of ethanol. The precipitate of compound **1** was collected by filtration and purified by recrystallization from toluene. The bromination of **1** (0.3 g, 0.23 mmol) with N-bromosuccinimide (0.082 g, 0.46 mmol) in 1,2-dichlorobenzene (40 mL) at room temperature within 3 h afforded monomer **M3** (0.32 g, 95%).

Compound **1**: $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ (ppm) 9.12 (d, 2H, $J = 4.2$ Hz), 7.98 (d, 2H, $J = 4.2$ Hz), 7.96 (d, 2H, $J = 3.6$ Hz), 7.79 (d, 2H, $J = 7.7$ Hz), 7.70 (d, 2H, $J = 7.7$ Hz), 7.33 (d, 2H, $J = 4.2$ Hz), 7.05 (t, 2H, $J = 3.7$ Hz), 4.1 (d, 4H, $J = 7.7$ Hz), 2.0 (m, 2H), 1.17–1.40 (m, 64H), 0.80 (m, 12H); $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ (ppm) 161.42, 152.30, 152.20, 144.01, 139.51, 139.06, 136.51, 131.16, 127.98, 127.76, 127.43, 127.14, 126.73, 125.73, 125.22, 124.43, 108.72, 46.56, 38.37, 31.95, 31.44, 30.31, 29.80, 29.72, 29.42, 26.48, 22.70, 14.12

Compound **M3**: $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ (ppm) 9.13 (d, 2H, $J = 4.2$ Hz), 8.10 (d, 2H, $J = 4.3$ Hz), 7.90 (d, 2H, $J = 7.7$ Hz), 7.80 (d, 2H, $J = 4.0$ Hz), 7.75 (d, 2H, $J = 7.7$ Hz), 7.08 (d, 2H, $J = 4.0$ Hz), 4.10 (d, 4H, $J = 8.1$ Hz), 2.02 (m, 2H), 1.20–1.40 (m, 64H), 0.83 (m, 12H); $^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ (ppm) 161.39, 152.25, 152.12, 144.03, 140.55, 139.64, 136.68, 131.43, 130.84, 127.93, 127.72, 125.95, 125.84, 124.94, 124.75, 115.57, 109.00, 46.51, 38.44, 32.14, 31.49, 30.48, 29.97, 29.91, 29.62, 26.60, 22.95, 14.31.

The polymer **P2** was synthesized similarly to **P1** using monomers **M1** (0.245 g, 0.21 mmol) and **M3** (0.3 g, 0.21 mmol). The amount of catalyst tetrakis(triphenylphosphine)palladium(0) was reduced to 5 mg (0.0043 mmol) in this case. The molecular weight characteristics of the formed polymer were regularly monitored and the reaction was terminated when the weight average molecular weight M_w was increased to 100 kDa. Polymer **P2** was purified and isolated in the same way as **P1**. The total yield of the purified **P2** was 86%. $M_w = 144$ kDa, $M_w/M_n = 1.8$.

2.3. Spectral and electrochemical measurements

Cyclic voltammetry measurements were performed for the polymers following the procedure reported in [19]. Absorption spectra were recorded using an Avantes AvaSpec-2048 optical fibre spectrometer.

2.4. Device preparation and characterization

The P1 and P2 copolymers were mixed with the commercial (6,6)-phenyl-C61-butyric acid methyl ester ([60]PCBM) from Ossila, and the blends were used to prepare the devices. The titanium oxide (TiO_x) material was synthesized using the sol-gel chemistry, according to a synthesis procedure described in ref [20].

All the photovoltaic cells and photodetectors fabrication was performed under a controlled nitrogen atmosphere (inside a glove-box), except for the deposition of the first poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) layer and the TiO_x precursor, as described below. The TiO_x layer was used to decrease the dark current and to improve the photocurrent response (see Supplementary Material S2).

The devices were produced on standard Ossila glass substrates covered with ITO transparent electrode (20 \square /sq.). Their layered structure was ITO/PEDOT:PSS (30 nm)/(P1 or P2)/[60]PCBM (50 nm)/

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