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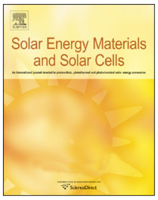

Solubilized 5,6-bis(octyloxy)benzoxadiazole as a versatile acceptor block for designing novel (-X-DADAD-)$_n$ and (-X-DADADAD-)$_n$ electron donor copolymers for bulk heterojunction organic solar cells

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ABSTRACT

Three novel conjugated polymers incorporating extended DADAD and DADADAD building blocks with the 5,6-bisalkoxybenzoxadiazole acceptor (A) and the electron donor (D) thiophene units were synthesized and fully characterized. The application of the benzoxadiazole instead of benzothiadiazole resulted in a significant increase in the open circuit voltage of organic solar cells based on such polymers. The best performing material delivered a decent solar light power conversion efficiency of 5.5% in organic bulk heterojunction solar cells using $PC_{71}BM$ as an electron acceptor component. The obtained results revealed a high potential of using different acceptor building blocks in the design of novel (-X-DADAD-)$_n$ polymers with tailored optoelectronic and photovoltaic properties.

1. Introduction

Development of the solar energy harvesting technologies is a crucial research direction in the view of the growing energy demands of the modern society. Continuous combustion of fossil fuel for energy production results in severe ecological side effects and might leave our future generations without essentially important natural resources, required e.g. for chemical industry. Among different types of photovoltaic technologies organic solar cells attracted much attention because of easy processing, low cost, lightweight, flexibility and possibility of fine-tuning of electronic properties of organic photoactive materials [1,2]. Organic solar cells based on polymer-fullerene blends are now reaching the efficiencies up to 10% due to development of novel materials and optimization of the device architectures [3–6].

Vast majority of highly efficient photoactive materials belong to the push-pull group of polymers which comprise electron-rich (donor) and electron-deficient (acceptor) units in their molecular backbone [7–11]. An appropriate combination of donor and acceptor blocks enables tuning the energy levels and energy band gaps of polymers providing solar cells with enhanced open circuit voltage (V_{OC}) and short circuit current density (J_{SC}).

Recently, we have proposed a promising approach for designing a new family of (-X-DADAD-)$_n$ donor-acceptor conjugated copolymers. In particular, conjugated polymers comprising carbazole (X) moieties bearing solubilizing alkyl chains, thiophene (T) donor units (D) and benzothiadiazole (BT) acceptor fragments (A) were reported [12,13]. The application of the extended T-BT-T-BT-T building block (as compared to the conventional T-BT-T) allowed us to reduce significantly the energy band gap of the resulting polymer (from 1.90 to 1.65 eV) while keeping the HOMO level almost unchanged (-5.50 eV vs. -5.44 eV). It has been also shown recently that optoelectronic properties of statistical carbazole-fluorene-T-T-BT-T-BT-T-T polymers can be tailored by changing the carbazole/fluorene ratio [14].

It is notable that the designed carbazole-(fluorene)-thiophene-benzothiadiazole copolymers demonstrated an excellent photochemical stability in thin films and in devices [12]. Additionally, novel materials enabled fabrication of flexible plastic solar cells with the efficiencies of 5–6% [15]. These examples suggest that the developed (-X-DADAD-)$_n$ polymers might find industrial applications in the production of large area organic solar modules demonstrating acceptable efficiencies and long-term operation stability.

It should be emphasized that the proposed (-X-DADAD-)$_n$ polymer architectures were explored by now only using benzothiadiazole (BT) as an acceptor (A) unit. However, the

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application of different acceptor units opens wider opportunities for designing novel conjugated polymers for efficient organic photovoltaics. In particular, a further improvement of the optoelectronic properties of these polymers might be achieved by replacing the sulfur atom in benzothiadiazole unit with oxygen. It is known that introduction of the benzoxadiazole (BO) units to the polymer chain increases the oxidation potential of the material (reduces HOMO energy) and tends to increase the open circuit voltage of the solar cells [16,17,18]. Additionally, BO-based polymers usually are more crystalline and demonstrate higher charge carrier mobilities in comparison with the BT-based analogues [18,19]. However, a high crystallinity might also cause low solubility of the BO-containing polymers challenging their processing and leading to a non-optimal morphology of the polymer-fullerene blend films [20,21,22]. This problem was partially solved by application of soluble 5,6-bis(alkoxy)-substituted BO as an acceptor block [23,24]. The polymers comprising the benzoxadiazole units modified with alkoxy groups are currently the most efficient BO-based materials demonstrating the solar cell power conversion efficiencies up to 8% [25,26].

In the present work we have designed and explored the first (-X-DADAD-)$_n$ copolymers bearing 5,6-bis(octyloxy)-benzo[*c*][2,1,3]oxadiazole as acceptor moieties. The application of the solubilized acceptor units allowed us to synthesize polymers, incorporating extended T-BO-T-BO-T (P1), T-BO-T-BO-T-BO-T (P2) and T-T-BO-T-BO-T-T (P3) molecular architectures (Fig. 1).

2. Experimental

2.1. Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures. AFM images were obtained using an NTEGRA PRIMA instrument (NT-MDT, Russia). Absorption spectra (for solutions of polymers in DCB and thin films) were obtained using an Avantes AvaSpec-2048 optical fiber spectrometer.

Molecular weight characteristics of conjugated polymers were obtained using a Shimadzu LC20 instrument equipped with a Phenomenex Luna Phenogel 5u column (0.78 × 30 cm, 5–500 kDa). The measurements were performed using freshly distilled toluene as an eluent (flow rate 0.5 mL min^{-1}, column temperature 50 °C). The column was calibrated using a series of custom-made F8BT standards with PDI <1.5 (toluene used as eluent). Molecular weights of the F8BT standards were crosschecked additionally using a "Waters Alliance GPCV 2000" instrument equipped with a multi-angle scattering detector HELEOS II (Wyatt).

Purification of low molecular weight compounds (key building blocks) was performed using preparative GPC at Shimadzu LC20 instrument equipped with a Shodex GPC K-2001 50 Å 6 μm, (20.0 × 300 mm). Freshly distilled toluene was used as an eluent (flow rate 1 mL min^{-1}, column temperature 40 °C).

Synthesis of 4,7-dibromo-5,6-bis(octyloxy)benzo[*c*][2,1,3]oxadiazole **1** was performed according to the previously reported procedure [27].

2.1.1. Synthesis of 2 and 4

Compound **1** (2.0 g, 3.76 mmol), 2-(tributylstannyl)thiophene (0.85 g, 1.27 mmol) and 2,5-bis(tributylstannyl)thiophene (3.35 g, 9.04 mmol) were dissolved in anhydrous toluene (50 mL) in a three necked round-bottom flask. The mixture was deaerated and Pd(PPh$_3$)$_4$ (0.023 g, 0.02 mmol) was added under argon. The mixture was heated at reflux for 24 h and then cooled to the room temperature. The target compounds **2** (0.428 g, 33%) and **4** (0.114 g, 12%) were separated from the 5,6-bis(octyloxy)-4,7-di(thiophene-2-yl)benzo[2,1,3]oxadiazole side product (yield 1.02 g, 52%) by column chromatography on SiO$_2$ (light petroleum-toluene as eluent) and further purified by preparative GPC.

Compound 2: yield 33% ^{1}H NMR (CDCl$_3$, 600 MHz): δ (ppm)

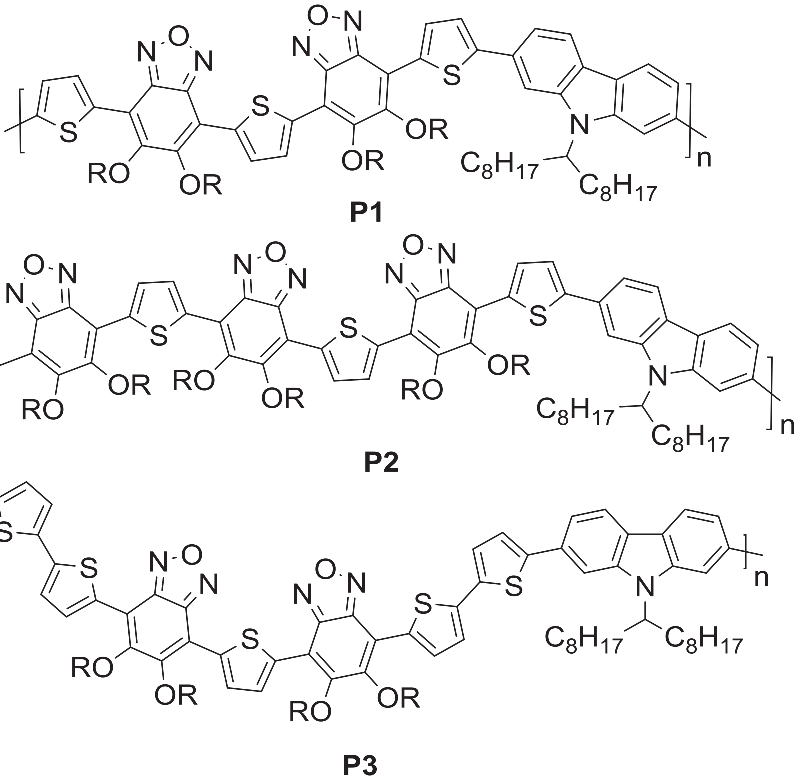

Fig. 1. Molecular structures of P1-P3.