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Synthesis of benzodithiophene and bithiazole based copolymer and its transistor property

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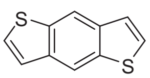
ABSTRACT

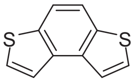
To extract improved charge carrier mobility from a benzo[1,2-*b*:4,3-*b*′]dithiophene (BdT) based polymer, **PDodBdTBTz** was synthesized by directly attaching 7,8-didodecyloxybenzo[1,2-*b*:4,3-*b*′]dithiophene (BdT-Dod) and 4,4′-dibutyl-2,2′-bithiazole (BTz) by Pd(II)-catalyzed Stille polymerization and characterized by ^{1}H NMR and UV–vis spectroscopy, GPC, CV, TGA, DSC and AFM. The copolymer exhibited a p-type mobility of $\sim 10^{-5}$ cm^2 V^{-1} s^{-1} that improved to 7.6×10^{-3} cm^2 V^{-1} s^{-1} after annealing at its T_c of 230 °C. This is the highest value of hole mobility among any benzo[1,2-*b*:4,3-*b*′]dithiophene (BdT) containing polymer and more than 10 times higher than any previous report of hole mobility from any BdT based polymer.

1. Introduction

A plethora of conjugated polymers have been reported after the discovery of the synthetic metal in 1977 [1] and applied in several organic electronic devices; especially, polymer field effect transistors (PFETs), polymer solar cells (PSCs), polymer light emitting diodes (PLEDs), polymer electrochromic devices (PECDs). Thiophene based polymers have been a centre of research in organic electronics. Among these, benzo[1,2-b:4,5-*b*′]dithiophene (BDT) based polymers were prepared and reported as a potent candidates for the application in variety of electronic devices [2–4]. On the contrary, benzo[1,2-*b*:4,3-*b*′]dithiophene (BdT), which is another isomer of BDT, has received scant attention [5]. We have recently reported two BdT-Dod based polymers, which exhibited electrochromic switching within low potential window. Particularly, the copolymer containing BdT-Dod and selenophene exhibited the coloration efficiency of 100 C cm^{-1} [6].



benzo[1,2-b:4,5-b']dithiophene
(BDT)



benzo[1,2-b:4,3-b']dithiophene
(BdT)

Sasaki and co-workers [7] reported the fabrication of OLEDs using 1,2-dithienylethylene derivatives including benzo[1,2-*b*:4,3-*b*′]dithiophene (BdT). Li and co-workers [4] obtained a power conversion efficiency (PCE) as high as 3.40% from 7,8-didodecyloxybenzo[1,2-*b*:4,3-*b*′]dithiophene (BdT-Dod) based polymers. The copolymer of thiophene-capped BdT-Dod with 4,4′-dibutyl-2,2′-bithiazole (BTz) exhibited a PCE of 2.81 and a space-charge limited current (SCLC) mobility of 5.53×10^{-4} cm^2 V^{-1} s^{-1} [4]. Incorporation of BTz in main conjugated core of a polymer chain often improves (i) planarity, (ii) π-stacking, and (iii) non-covalent interactions between the chalcogen (S) and N that enhances the inter-chain interactions also with the

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transfer integral [8,9]. Recently, a significant improvement in transistor performance was found in case of cyclopenta[*c*]thiophene (CPT) and BTz containing polymer, which was attributed to its semicrystalline nature [10]. This performance is the most superior among any CPT containing polymer reported till date. Mullen and co-workers reported a series of benzodithiophene based polymers with different degrees of curvature along the polymer backbone [11]. BdT based polymer showed the strongest curvature and displayed weak ordering along with poor p-type field effect mobility (μ_{FET}). The highest μ_{FET} in the order of only 10^{-4} was reported from any BdT based polymer till this report.

In these regards, we have synthesized BdT and BTz based copolymer by direct fusion (without any conjugated spacer) and characterized it both by its optoelectronic and transistor properties.

2. Experimental

2.1. Materials

All reagents were purchased commercially and used without further purification except THF and toluene, which were dried over sodium/benzophenone prior to use. Dichloromethane was dried over calcium hydride and distilled before the CV experiment. Pyridine was also dried over solid KOH and distilled before reaction.

2.2. Material characterization

^{1}H NMR spectrum was recorded on JEOL ECS 400 spectrometer. UV–vis absorption spectra were recorded on a HITACHI U-4100 UV–vis–NIR spectrophotometer. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were determined by gel permeation chromatography (GPC) on a WATERS 2414 module, calibrated with polystyrene standard and THF as eluent at a flow rate of 1 mL/min at rt. TGA for the polymer was operated under nitrogen at a heating rate of 10 °C/min using Mettler Toledo TGA/SDTA 851. DSC was performed on Mettler Toledo DSC 1 at a heating/cooling rate of 10 °C/min under nitrogen. The photoluminescence measurements were done with the Horiba Jobin Yvon Fluoromax-3. CV was performed on a Princeton Applied Research 263A potentiostat with a three-electrode cell in dry acetonitrile at a scan rate of 50 mV s^{-1} under nitrogen atmosphere. The measurement was calibrated using ferrocene as standard. Topographic images and phase images were taken using AFM with an NT-MDT instrument, model no. AP-0100 in tapping-mode.

The electrical characterization of the transistor devices were done with two identical source meters (Keithley 2400) and a high impedance electrometer (Keithley 6514) and were cross checked with measurements from a standard Keithley 4200 semiconductor parameter analyzer. The mobility values reported are the median values, from the measurements performed on a large number of devices (~10–15 devices of the polymer).

2.3. Synthesis of **PDodBdTBTz**

4,4′-Dibutyl-5,5′-bis(trimethylstannyl)-2,2′-bithiazole (**1**) [10] (177 mg, 0.25 mmol) and 2,5-Dibromo-7,8-didodecyloxybenzo[1,2-b:4,3-b′]dithiophene (**2**) [4] (150 mg, 0.25 mmol) were dissolved in 30 mL dry toluene, kept in a three-necked flask and thoroughly purged with nitrogen for 30 min before addition of $Pd_2(dba)_3$ (26 mg, 0.025 mmol) and P(*o*-tolyl)$_3$ (15 mg, 0.05 mmol). The mixture was then refluxed for 43 h. The reaction mixture was cooled to room temperature and the crude polymer was precipitated out by addition of excess (about 3 times of the volume of reaction mixture) methanol. The mixture was acidified by addition of 2 mL of concentrated hydrochloric acid and stirred for 1 h at rt. The precipitate was collected by filtration to afford crude polymer, which was further purified by washing with methanol and acetone, respectively for 48 h in a Soxhlet apparatus to remove the oligomers and catalyst residues. The polymer was then dried in vacuum for 3 h. Finally, **PDodBdTBTz** (121 mg, 58%) was obtained after drying. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (br, 2H), 4.30 (br, 4H), 3.08 (br, 4H), 1.86–1.73 (br, 8H), 1.25 (br, 40H), 0.99–0.87 (br, 12H).

3. Results and discussion

We have synthesized a new copolymer **PDodBdTBTz**, containing BdT-Dod and BTz by Stille coupling starting from the dibromo derivative of BdT-Dod **2** and distannyl derivative of BTz **1** in toluene using $Pd_2(dba)_3$ as catalyst (Scheme 1). **PDodBdTBTz** was highly soluble in common organic solvents like dichloromethane, chloroform, chlorobenzene, tetrahydrofuran. It exhibited M_n and M_w of 13 and 23 kDa, respectively and a polydispersity index (PDI) of 1.8 versus polystyrene standards upon evaluation by GPC using THF as eluent. The obtained M_n of 13 kDa corresponds to the degree of polymerization of 16.

3.1. Thermal analysis of **PDodBdTBTz**

Upon heating under nitrogen **PDodBdTBTz** lost its 5% of weight at 348 °C (Fig. 1a). BdT unit with fused ring is known to increase the structural rigidity to ensure high thermal stability [12]. Thermal stability of the resulting copolymer could prevent the degradation under high temperature annealing condition of the electronic devices [13]. **PDodBdTBTz** exhibited a local crystallization (T_c) at 230 °C in DSC (Fig. 1b), which signifies the formation of crystalline or ordered domains in the bulk. So thermal annealing of the polymers at T_c during device fabrication could improve the supramolecular arrangements of the polymer chains resulting in higher charge carrier mobility than that of un-annealed film of **PDodBdTBTz**.

3.2. Optical properties of **PDodBdTBTz**

To measure the optical band gap (E_g^{opt}) for **PDodBdTBTz**, UV–vis spectra of the polymer was taken in both solution and film states (Fig. 2). Thin film was prepared by spin coating the polymer on an ITO-coated glass (premodified