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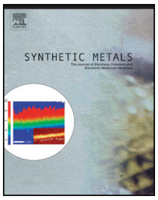

Short Communication

# Synthesis of n-type semiconducting polymer consisting of benzodipyrrolidone and thieno-[3,4-*c*]-pyrrole-4,6-dione via C—H direct arylation

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ABSTRACT

Direct arylation polycondensation of 3,7-bis(4-bromophenyl)-1,5-bis(2-octyldodecyl)benzo[1,2-*b*:4,5-*b*′]dipyrrole-2,6(1*H*,5*H*)-dione with 5-(2-ethylhexyl)-thieno-[3,4-*c*]-pyrrole-4,6-dione gave the corresponding benzodipyrrolidone-based conjugated polymer with a molecular weight of 147,000 in 92% yield. The optical and thermal properties of the polymer were evaluated. The polymer showed n-type semiconducting behavior in organic field-effect transistors with an electron mobility of $1.3\pm0.2\times10^{-3\,\mathrm{cm}2}\mathrm{V}^{-1}\,\mathrm{s}^{-1}$.

## 1. Introduction

Polycondensation via direct C—H arylation has been recognized as an effective method for the practical synthesis of π-conjugated polymers because the reaction process eliminates the prior preparation of organometallic reagents and the treatment of metal-containing byproducts [1]. Recently, several groups have attempted to utilize this reaction for the synthesis of π-conjugated polymers for use as semiconducting materials for optoelectronic devices such as organic photovoltaic cells (OPVs) [2,3], organic field effect transistors (OFETs) [3,4], and light emitting diodes [5]. Among these π-conjugated polymers, copolymers containing naphthalene diimide serve as n-type semiconducting materials in OFETs [4b,d,e,6].

In the context of n-type semiconducting polymers, the benzo[1,2-*b*:4,5-*b*′]dipyrrole-2,6(1*H*,5*H*)-dione unit, also known as benzodipyrrolidone (BDP), has attracted attention owing to its excellent electron-accepting property and planar conjugated lactam structure, resulting in a lowered LUMO level and improved thermal stabilities of its π-conjugated polymers [7]. BDP-based polymers thus serve as n-type semiconducting materials and/or as donor-acceptor low bandgap polymers for the fabrication of OFETs and OPVs. Such polymers have been synthesized by the Suzuki-Miyaura and Migita-Kosugi-Stille cross-coupling polycondensation reactions. Owing to the high potential of BDP-based polymers, we have examined direct arylation polycondensation of 3,7-bis(4-bromophenyl)-1,5-bis(2-octyldodecyl)benzo[1,2-*b*:4,5--*b*′]dipyrrole-2,6(1*H*,5*H*)-dione ($Br_2$-BDP) with 5-(2-ethylhexyl)-thieno-[3,4*c*]-pyrrole-4,6-dione (TPD). TPD is an appropriate choice of coupling partner for BDP because TPD possesses good reactivity toward direct arylation polycondensation and serves as an electron-accepting unit in the π-conjugated polymers [2a,b,8]. We herein report the synthesis of a π-conjugated BDP-TPD polymer via direct arylation polycondensation, and also describe the physical properties and semiconducting behavior of the polymer.

## 2. Experimental

### 2.1. Materials

*p*-Phenylenediamine, 4-bromo-DL-mandelic acid, 2-octyldodecanol, $Pd(OAc)_2$, $Cs_2CO_3$, pvalic acid (PivOH), tricyclohexylphosphonium tetrafluoroborate ($PCy_3\cdot HBF_4$), and other chemicals were received from commercial suppliers and used without further purification. Anhydrous toluene was purchased from Kanto chemical and used as a dry solvent. $Br_2$-BDP [7] and TPD [9] were prepared with references to procedures reported in the literatures.

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### 2.2. General measurements and characterization

NMR spectra were recorded on Bruker AVANCE-600 and AVANCE-400 NMR spectrometers. Gel permeation chromatography (GPC) measurements were carried out using a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using $CHCl_3$ as an eluent after calibration with polystyrene standards at 40 °C. Ultraviolet visible absorption spectra of the spin coated thin films were recorded on a JASCO V-630 spectrophotometer. The HOMO energy level was estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki AC-3 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer. X-ray diffraction patterns were recorded at 298 K on a Rigaku model Multi-Flex X-ray diffractometer with a CuKα radiation source. The thermal properties were measured on an EXSTAR TG/DTA6300 instrument. The surface morphology of the BDP-TPD film was observed using an atomic force microscopy (AFM) (Hitachi High-Tech Science 5100N). Thermogravimetric (TG) analysis was carried out using a Seiko Instruments Inc. TG/DTA7300 systems. All the manipulations for the reactions were carried out under a nitrogen atmosphere using a glove box or standard Schlenk technique.

### 2.3. Synthesis

A mixture of $Pd(OAc)_2$ (0.89 mg, 0.0040 mmol), $PCy_3 \cdot HBF_4$ (1.47 mg, 0.0040 mmol), PivOH (6.9 μL, 0.060 mmol), $Cs_2CO_3$ (130 mg, 0.40 mmol), $Br_2$-BDP (211 mg, 0.20 mmol), and TPD (53 mg, 0.20 mmol) was stirred in anhydrous toluene (1.0 mL) for 24 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into methanol and the precipitate was separated by filtration and washed with an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8), 0.1 M HCl solution, distilled water, methanol, and hexane. The precipitate was dissolved in $CHCl_3$ and the solution was filtered through a plug of Celite to remove insoluble material. A reprecipitation from $CHCl_3$/methanol gave a polymeric product as a purple black solid. The product was purified by Soxhlet extraction with toluene and then finally collected with $CHCl_3$ to give BDP-TPD polymer in 92% yield. $M_n = 147{,}000$, $M_w/M_n = 2.65$. $^1H$ NMR (600 MHz, 353 K, $C_2D_2Cl_4$): $\delta$ 8.33 (s, 4H), 7.93 (s, 4H), 6.48 (s, 2H), 3.60 (s, 6H), 1.91 (s, 3H), 1.54 (s, 4H), 1.50-1.20 (m, 72H), 1.05-0.95 (m, 6H), 0.88 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, 353 K, $C_2D_2Cl_4$): $\delta$ 162.8, 151.0, 144.6, 144.0, 134.9, 131.4, 129.9, 128.3 126.2, 120.2, 118.5, 44.2, 37.1, 31.9, 31.7, 30.7, 29.8, 29.5, 29.4, 29.1, 28.6, 26.6, 24.1, 22.9, 22.5, 13.9, 10.5. Anal. Calcd. for $C_{78}H_{111}N_3O_4S$: C, 78.50; H, 9.62; N, 3.61. Found: C, 78.08; H, 9.46; N, 3.68.

### 2.4. Fabrication and characterization of OFET

To estimate the electron mobility of the polymer, OFETs with a top-contact geometry were fabricated and characterized as follows. A glass/Au gate electrode/Parylene-C insulator substrate was prepared according to the previously reported methods [10]. The BDP-TPD polymer was spin-coated from *o*-dichlorobenzene solution onto the Parylene-C layer and the coated substrate was dried for 10 min at 110 °C in a $N_2$-filled glove box. Ag (40 nm) source-drain electrodes were thermally evaporated onto the substrates through shadow masks. The channel length and width were fixed at 75 μm and 5 mm, respectively. The OFET measurements were conducted using a Keithley 2636A System Source Meter. In OFETs measurements, five devices were characterized to obtain an average value with the standard deviation. OFETs consisting of glass/Au gate electrode/Parylene-C insulator/BDP-TPD polymer/Au source-drain electrodes were also fabricated for estimating the p-type semiconducting characteristics.

## 3. Results and discussion

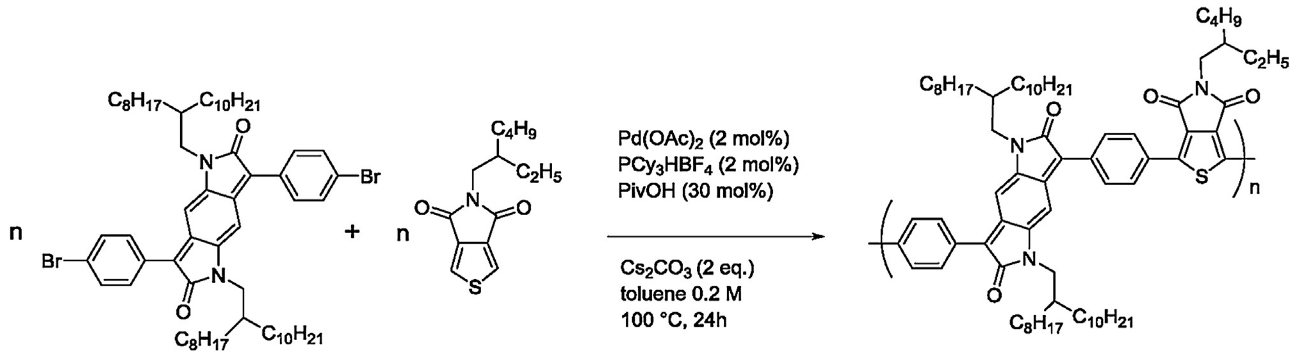
### 3.1. Synthesis and characterization

The polycondensation of $Br_2$-BDP with TPD via direct arylation was conducted under the optimal conditions described in a previous report [8f]. The polycondensation reaction afforded the corresponding BDP-TPD polymer with a molecular weight of 147,000 in 92% yield (Scheme 1). Owing to the introduction of long alkyl chains, the obtained polymer exhibits good solubility in $CHCl_3$, 1,1,2,2-tetrachloroethane, and *o*-dichlorobenzene.

The chemical structure of the BDP-TPD polymer was characterized by NMR spectroscopy and elemental analysis. As shown in Fig. 1, each $^1H$ NMR signal can be assigned to the repeating unit; the integral ratios of the signals agree with the assignments and are consistent with the alternating structure of the polymer. The signal of the terminal C—H moiety of the TPD unit at 7.01 ppm was scarcely observed in the $^1H$ NMR spectrum because of its high molecular weight, and other minor signals assigned to the structural defects were not observed. All $^{13}C\{^1H\}$ signals were also assigned to the carbons in the recurring unit (Fig. S1, Supplementary data).

### 3.2. Physical and chemical properties

The UV–vis absorption spectra of the BDP-TPD polymer and the reference polymer (F-TPD, Scheme 2) [8f] are shown in Fig. 2. Owing to the presence of the BDP unit, the polymer exhibits absorption in the long wavelength region, with the $\lambda_{max}$ at 592 nm



**Scheme 1.** Synthesis of BDP-TPD polymer.