

Charge Transport Behaviours of End-Capped Narrow Band Gap Polymers in Bottom-Contact Organic Field-Effect Transistors†

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Experimental

Synthesis

5,5'-Bis(trimethylstannyl)-3,3'-Di-n-dodecylsilylene-2,2'-bithiophene (**M1**) and 4,7-dibromo-2,1,3-benzothiadiazole (**M2**) were prepared via literature procedures.

Polymerization and end functionality modification

To get the specific M_n , stoichiometric ratio of distannated monomer (**M1**) and dibromo monomer (**M2**) was adjusted. The ratios of **M1** and **M2** were 1:1, 1.035:1, 1.045:1 and 1.06:1. Except the ratio, general procedure was followed as described below. The exact weights of all chemicals were measured in a glovebox. To each microwave tube was added 300 mg and the amount of **2** which was determined by the stoichiometric ratio was added into the tubes. After that, 13 mg of $\text{Pd}(\text{PPh}_3)_4$ and 2 ml of xylenes was added to each microwave tube. Then, the tubes were sealed inside of the glovebox and subjected to the following reaction conditions in a microwave reactor: 120 °C for 5 min, 140 °C for 5 min and 170 °C for 40 min. The resulting products were precipitated in methanol and filtrated. The residual solid was loaded into an extraction thimble and washed successively with hexanes (4 h), THF (12h) and acetone (30 min.) and then insoluble portion of THF was collected. The polymers were dried in vacuo, then analysed via GPC. This led to **P1** with M_n values of 20 kg/mol, 28 kg/mol, 32 kg/mol and 26 kg/mol as the equivalents of **M1** increased from 1.00 to 1.06 equivalents and each PDI was 1.9, 2.2, 2.4 and 2.3 respectively.

For end group modification, the specific stoichiometric ratios of **M1** and **M2** were determined same as **P1** and polymerized by following the general procedure as described above. After polymerization, the microwave tube was transferred into glovebox and degassed 4 equivalent of 2-bromothiophene for **1** was added in the tube to modify the stannyl side and subjected to the same polymerization condition. Then, the tube was transferred into glovebox again and degassed 8 equivalent 2-(tributylstanny)thiophene to modify bromine side was

added in the tube and run microwave at the same condition as polymerization again. The product was precipitated in methanol and filtrated. The residual solid was soxhleted successively with hexanes (4 h), methylene chloride (16h) and acetone (30 min.). The polymers were dried in vacuo, then analysed via GPC. This led to **P2** with Mn values of 20 kg/mol, 26 kg/mol, 30 kg/mol and 25 kg/mol as the equivalents of **M1** increased from 1.00 to 1.06 equivalents and each PDI was 1.9, 2.2, 2.1 and 2.2. **P2** wasn't soxhleted with THF since the polymer was too soluble in THF.

Materials: Our focus is on the poly[(4,4-didodecyldithieno[3,2-b :2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (P1). The first, P1 was prepared via microwave-assisted Stille cross coupling polymerization, as reported in the literature. PDTBT thus likely contains residual unreacted stannyl and bromide end groups. As a comparison, the 2-bromothiophene and 2-(tributylstanny) thiophene end group (P2) was studied (Scheme 1??). Substantial efforts were dedicated to obtain P1 and P2 in sufficiently similar average molecular weights in order to make a fair comparison of their performance in devices. The specific sample used in our studies had a number average molecular weight of 10 and 30 kg/mol and a molecular weight distribution with a polydispersity of 2.1.

Device Preparation: OFETs with a bottom-gate, bottom-contact geometry were fabricated by using heavily doped n-type Si wafers as the gate electrodes and a 150 nm-thick thermally grown silicon dioxide (SiO₂) layer (capacitance = 20 nF cm⁻²) as the gate dielectric. Using conventional photolithography, the gold source and drain electrodes were structured in bottom-contact transistors with 10 μm channel length and channel width 1000 μm. A 3 nm-thick of titanium layer was used for an adhesion of the gold electrodes. Initially, the substrates were cleaned by rinsing with acetone, ethanol for 15 min. After blown dry with N₂, the substrates were treated with UV-ozone for 15 min. The SiO₂ surface was treated with

hexamethyldisilazane (HMDS). HMDS was used as an organic interlayer material to reduce interface charge trapping, and spin-cast on the SiO₂ substrate at a speed of 1500rpm for 60s. P1 and P2 dissolved in chlorobenzene (10 mg mL⁻¹) at room temperature. A chlorobenzene solution was spin coated at 2500 rpm onto the pre-patterned source/drain electrodes. All films were fabricated inside a nitrogen atmosphere glovebox.

Characterization: An atomic force microscope (AFM, Multimode IIIa, Digital Instruments) was used to characterize the surface morphologies of the samples. Organic semiconductor solution was coated on the glass for UV-vis. study. The solid state UV-vis. absorption spectra were recorded on a Cary 5000 (Varian) spectrophotometer. Synchrotron-based GIXD experiments were performed on various semiconductor films at beamline 3C and 9A at the Pohang Accelerator Laboratory in Korea. The electrical characteristics of the OFETs were measured in the accumulation mode by using Keithley 4200 source/measure units with a step voltage of 1.0 V, a sweep delay of 0 s, and a hold time of 0 s inside a nitrogen atmosphere glovebox at room temperature.