



Morphological control of conjugated polymers by additive annealing for solar cell applications



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ABSTRACT

A novel conjugated polymer, PVBT, having a D-A type alternating configuration is synthesized for organic photovoltaic application. It exhibits a bimodal-shaped absorption because of intramolecular charge transfer. Comparison of absorption intensity both in the long and the short wavelength region indicates decent chain planarity of PVBT. Organic photovoltaic devices made of PVBT exhibit better performance compared to identical devices from PVTT having a similar chemical structure due to a deeper HOMO energy level and a lower band-gap of PVBT. Additive assisted annealing further improves the device performance, and film morphology analysis reveals the importance of nano-dimensional phase separation to suppress inner-domain recombination.

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1. Introduction

The aggregation behavior of conjugated polymer (CP) has drawn great attentions because of its effect on the optoelectronic properties of CPs in the solid state [1–10]. For example, aggregation of CP improves electrical charge mobility, which can ultimately lead to promising improvements both in organic thin-film transistors (OTFTs) [4–6] and organic photovoltaic (OPV) devices [7–10]. However, it has been reported that CPs exhibiting strong aggregation behavior also augment charge recombination around the interface with PCBM derivatives, resulting in relatively lower V_{oc} than an expected value in OPV devices [11,12]. In other words, although a strongly aggregating CP may provide better charge mobility, photovoltaic performance cannot be reasonably optimized unless recombination is controlled to obtain a high V_{oc} .

A planar chain-conformation has been identified as a molecular feature providing a driving force for CP aggregation by promoting strong aromatic inter-chain interactions between CP backbones. However, it is not straightforward to precisely predict aggregation tendency among CPs sharing similar chemical structures. Recently, we reported a novel CP, PVTT, that has a strong aggregation tendency and often forms an aggregation-induced gel [12]. Its OPV

performance, however, was unexpectedly low because of charge recombination and the energy conversion efficiency became even worse after thermal annealing.

In this contribution, we designed and synthesized a novel CP, PVBT, having both a lower HOMO energy level for higher V_{oc} and an alternating electron donor (D)/acceptor (A) configuration for better light harvesting efficiency, respectively, than PVTT. Then, the film morphology of PVTT and PVBT was tuned, by means of additive assisted annealing method, to investigate the size effects of generated domain features on the device performance, such as charge recombination in bulk heterojunction type OPV devices.

2. Experimental

All starting materials were purchased from commercial suppliers (Aldrich and Fisher Sci.). Synthesized compounds were fully characterized with ¹H NMR and GC-mass, and molecular weights of the final polymers were measured with gel permeation chromatography (GPC) relative to polystyrene calibration standards.

2.1. 4,7-Bis(bromomethyl) benzo[c][1,2,5]thiadiazole (1)

Benzo[c][1,2,5]thiadiazole (3.16 g, 23.2 mmol) was dissolved in a mixture of 48% aqueous hydrobromic acid (100 mL) and glacial acetic acid (25 mL). Then, trioxane (10 g, 56 mmol) and trimethyl(tetradecyl) ammonium bromide (0.4 g) were added to the mixture. After refluxing for 24 h, the mixture was cooled,

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and the produced green solid was filtered. The collected solid was washed with water and ethanol, successively. The compound was recrystallized from toluene, to afford **3** (4.4 g, 59%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (s, 2H), 4.92 (s, 4H), and m/z EIMS 323.

2.2. Benzo[*c*][1,2,5]thiadiazole-4,7-dicarbaldehyde (**3**)

Compound **1** (3.32 g, 10.3 mmol) was taken in a round bottom flask along with sodium periodate (NaIO_4) (0.84 g, 4 mmol). The above mixture was dissolved in 30 mL of *N,N*-dimethylformamide (DMF) and heated at 150°C . The progress of the reaction was monitored by thin layer chromatography by comparison with the starting material (10% ethyl acetate in hexane). The reaction was completed within 50 min. The reaction mixture was cooled and treated with 20 mL of water and then extracted with diethyl ether. After the combined ether layers were dried over anhydrous magnesium sulfate (MgSO_4), column chromatography on silica gel (ethyl acetate/hexanes: 1:2) yielded compound **3** (1.48 g, 75%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.75 (s, 2H), 7.92 (d, 2H), and m/z EIMS 193.

2.3. PVBT

A solution of compound **2** (1 g, 1.575 mmol) and compound **3** (0.303 g, 1.575 mmol) in DMF was heated to 80°C . Potassium *tert*-butoxide (KOtBu) (0.47 g, 4.19 mmol) was added at once. The reaction mixture was stirred at 80°C for 4 h and then poured into water (100 mL). Purplish solid was filtered and washed with water and methanol several times. After redissolving collected solid into chloroform by heating, it was precipitated with methanol. Finally, residual monomers or oligomers were removed by Soxhlet extraction with methanol for 24 h (Mw 26 000; PDI 1.8).

2.4. Film preparation for OPV device

PCBM[70] was purchased from SES research and used without further purification. After dissolving obtained CPs (10 mg) and PCBM[70] (15 mg) into *o*-dichlorobenzene (1.0 mL), the mixture was filtered with a syringe filter (0.45 μm pore diameter) and used to form an active layer by means of spin-casting. In case of additive-assisted annealing, 1,8-octanedithiol (8.0 μL) was added to the CP:PCBM[70] blend solution, and the same procedure was used to obtain an active layer.

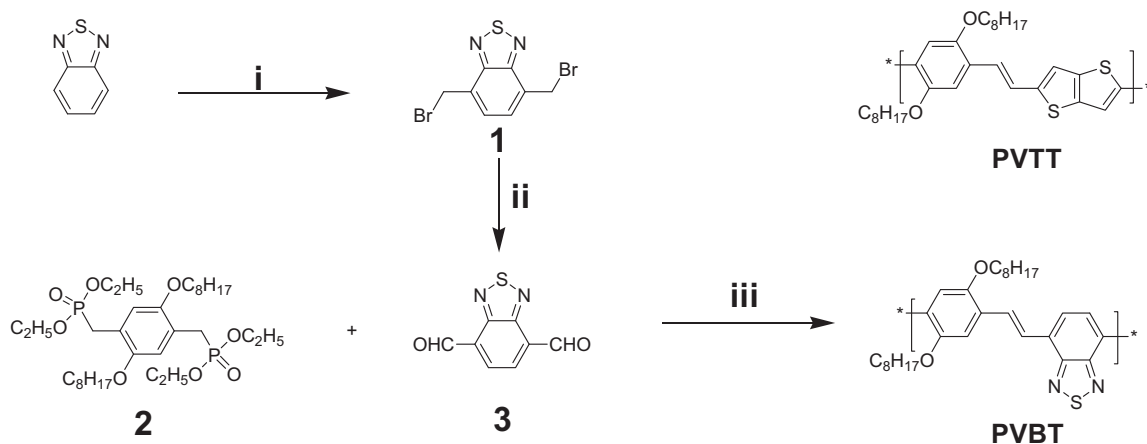
2.5. OPV device fabrication

ITO-coated glass was cleaned with acetone and IPA followed by UV ozone treatment for 10 min. PEDOT:PSS (Baytron PH 500) was spin-cast on the substrate and baked at 140°C for 15 min. CP:PCBM [70] blend solution was spin-cast at 700 rpm for 30 s and the blend film was used for metal electrode evaporation without further treatment. Final devices were fabricated by depositing 1-nm-thick LiF and 70 nm Al layer (9.6 mm^2), sequentially under 5×10^{-7} Torr (1 Torr = 133.32 Pa). All devices were characterized under nitrogen and the typical illumination intensity was 100 mW/cm^2 (AM 1.5G Oriel solar simulator).

3. Results and discussion

Detailed chemical structures and synthetic procedures for CPs investigated in this study are shown in Scheme 1. PVTT and 2,5-di-*n*-octyloxy-1,4-xylenediethylphosphonate ester (**2**) were obtained in previously described manners [12]. 4,7-Bis(bromo-methyl)-benzo[*c*][1,2,5]-thiadiazole (**1**) and benzo[*c*][1,2,5]thiadiazole-4,7-dicarbaldehyde (**3**) were obtained from electrophilic substitution and oxidation, respectively. Obtained compounds were fully characterized with $^1\text{H NMR}$ and GC-mass spectroscopy, and the final polymer, PVBT, was prepared from a Knoevenagel condensation using potassium *tert*-butoxide. In order to compare the optical properties of PVBT with PVTT, their absorption behavior was characterized with UV-vis absorption spectroscopy after film preparation.

As shown in Fig. 1a, PVBT exhibited a bimodal-shaped absorption, a characteristic absorption phenomenon in D-A type CPs. In general, the absorption of the shorter wavelength is originated from repeating units' molecular orbital hybridization under no intra-molecular charge transfer. CP chains become planar due to the intra-molecular charge transfer and consequently produce another absorption band in the longer wavelength region [13]. The absorption intensity of both the shorter and the longer wavelength regions can be tuned through manipulating intrinsic chain planarity of CPs. In general, the absorption intensity of the shorter wavelength relatively decreases compared to the absorption of the longer wavelength as CP chain planarity increases [13]. This implies that the obtained PVBT has decent chain planarity, which would promote π - π interaction and consequent inter-chain aggregation in the solid state. In addition, the absorption edge of PVBT became red-shifted about 50 nm, compared to PVTT, which would be more advantageous to harvesting broader solar



Scheme 1. Chemical Structures and detailed synthetic routes of PVBT. (i) HBr/acetic acid (4/1), trioxane, trimethyl(tetradecyl) ammonium bromide, reflux; (ii) NaIO_4 , DMF, 150°C ; (iii) KOtBu, DMF, 80°C .

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