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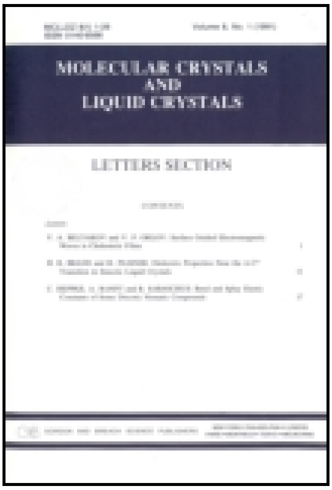

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Solution-Processable Organic Photovoltaic Cell Based on the Oligothiophene with Solubilizing β-alkyl Groups

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*We synthesized a linear π-conjugated small molecule (β-**DH5T**) based on thiophene, using the palladium-catalyzed Suzuki coupling. The oligothiophene was designed to contain β-substituted solubilizing alkyl groups to facilitate solution processing. The organic photovoltaic cell based on β-**DH5T**:$PC_{71}BM$ gave a power conversion efficiency of 0.46% with a short-circuit current of 4.69 mA/cm^2, an open-circuit voltage of 0.60 V, and a fill factor of 0.35, giving under AM 1.5G illumination (100 mW/cm^2). The optical and electrochemical properties and molecular alignment of oligothiophene were investigated using UV-visible absorption spectroscopy, cyclic voltammetry, and thin-film X-ray diffraction studies.*

Keywords Organic photovoltaic cells; solar cells; oligothiophene; small molecule; solution-processing

Introduction

Organic photovoltaic cells (OPVs) are promising sources of electrical power because of their low cost, and utility in renewable-energy applications[1,2]. Although most OPV cells with high performances (>8–10%) are based on bulk heterojunction polymer solar cells, small molecule-based OPV cells have recently attracted attention because of their well-defined molecular structures and ease of synthesis and purification[3]. Solution-processable small molecules are much easier to process than vacuum-deposited small molecules and much easier to synthesize than polymeric semiconductors. To date, most solution-processable small molecules with high OPV efficiencies have been based on oligothiophenes with various molecular shapes (e.g., linear, dendritic, star- or X-shaped)[7]. Oligothiophenes have been widely used in organic electronics such as organic field-effect transistors (OFETs) and OPV cells because they display high hole mobility and are easily chemically modified to tune their physical properties, such as molecular energy levels and band gaps. The physiochemical properties and solid-state structures of oligothiophenes have been varied by varying their substitution pattern[8,9]. In field of soluble small molecule-based OPVs, improvements in material solubility are central to achieving good film morphologies and

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high OPV efficiencies. The solubilities of small molecules have been improved by structural modifications such as introducing solubilizing alkyl groups or modifying the shapes of the backbones[10,11].

We previously developed the α-substituted rod-like oligothiophene (α**-DH5T**) as a donor material for OPV applications; [12] however, due to the poor solubility, the film morphology of α**-DH5T**, the α**-DH5T** film had poor morphology and homogeneity, and the solution-processed OPV devices prepared with α**-DH5T** did not display photovoltaic characteristics. In this work, we introduce a β-substituted alkyl group into the oligothiophene backbone to improve the material solubility, and evaluate the performance of oligothiophene as a donor in solution-processed photovoltaic cells. The optical and electrochemical properties as well as the molecular alignment of the oligothiophene are investigated using UV-visible absorption spectroscopy, cyclic voltammetry (CV), and thin film X-ray diffraction (XRD).

Experimental

Materials

2,2':5'.2"-Terthiophene, Aliquat®336, and tetrakis(triphenylphosphine)palladium(0) (Pd $(PPh_3)_4$) were purchased from Aldrich. 4-Hexyl-2-thiopheneboronic acid pinacol ester and (6,6)-Phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) was purchased from TCI ad Nano-C, respectively. All reagents purchased commercially were used without further purification, except for the toluene used as a solvent, which was dried over sodium/benzophenone.

Physical Measurements

Nuclear magnetic resonance (NMR) spectral data were obtained on a Bruker Avance spectrometer. Elemental analysis was performed with a CHNS-5 EA1108 elemental analyzer from Carlo ERBA Instruments. Differential scanning calorimetry (DSC) was performed on a TA instrument Q100 at heating and cooling rates of 10°C/min under a nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10°C/min using a Perkin Elmer TGA7 thermogravimetric analyzer. UV-visible spectra were obtained using a Shimadzu UV/vis. Spectrometer- and photoluminescence (PL) spectra were obtained using a Perkin Elmer spectrofluorometer. For CV measurement, the films were prepared by dip-coating the oligomer solution onto Pt wire and the measurements were calibrated using the ferrocene value of −4.8 eV as the standard. The highest occupied molecular orbital (HOMO) level was calculated using the empirical equation $I_p(\mathrm{HOMO}) = -(E_{\mathrm{onset}} + 4.39)$ where E_{onset} is the onset potential of oxidation[13].

Synthesis

5,5"-Dibromo-2,2':5',2"-terthiophene (1). 2,2':5'.2"-Terthiophene (1.20 g, 4.83 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF) 140 mL under nitrogen, and then, a solution of N-bromosuccinimide (NBS) (1.80 g, 10.14 mmol) in 10 mL of DMF was added dropwise by syringe to a stirred (0°C). After the reaction mixture being stirring at room temperature for 2 hours, an equal volume of water was added. The resulting mixture was extracted with chloroform, washed with sodium bicarbonate solution, dried over magnesium sulfate ($MgSO_4$), and evaporated, was obtained after drying in vacuum, resulting yellow solid (1.85 g; yield: 94.18%). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 6.99 (s, 2H); 6.97 (d, 2H); 6.91 (d, 2H).

4,7-Bis(4'-hexyl-2,2'-bithiophene-5-yl)thiophene (β-DH5T). 5,5"-Dibromo-2,2':5',2"-terthiophene (**1**, 0.50 g, 1.23 mmol), 4-hexyl-2-thiopheneboronic acid pinacol ester (0.87 g, 2.98 mmol), and the air-sensitive Pd(0) complex, tetrakis(triphenylphosphine)-palladium(0) ($Pd(PPh_3)_4$) (0.07 g, 0.06 mmol) were dissolved in distilled toluene. An aliquot of a 2 M aqueous sodium carbonate (2.45 mL, 4.90 mmol) and a phase-transfer catalyst, Aliquat®336 (0.05 g, 0.12 mmol), were purged in toluene under nitrogen and added dropwise to the mixture by syringe. The reaction mixture was then stirred and heated for 3 days under nitrogen. The reaction was cooled to room temperature, and the mixture was added dropwise to methanol. The precipitated solid was collected by filtration, and then purified by several reprecipitations in methanol, resulting in a shine yellow solid. Yield: 0.32 g (45.26%). ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 7.07 (s, 2H), 7.06 (d, 4H), 7.02 (d, 2H), 6.81 (d, 2H), 2.59 (t, 4H), 1.63 (q, 4H), 1.41-1.31 (m, 12H), 0.90 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.24, 136.88, 136.60, 136.03, 135.54, 125.17, 124.27, 124.22. 124.06, 119.29, 130.27, 130.10, 126.55, 124.23, 123.91 (two carbon), 31.67, 30.51 29.70, 28.97, 22.59, 14.07. Anal. Calcd for $C_{32}H_{36}S_5$: C, 66.16; H, 6.25; S, 27.60. Found: C, 65.45; H, 5.86; S, 29.64.

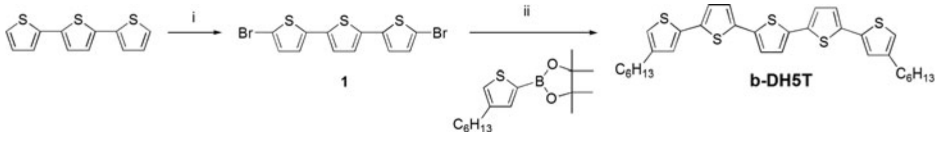
OPV Device Fabrication

The organic photovoltaic devices were fabricated with the configuration ITO/PEDOT:PSS (40 nm)/oligomer:$PC_{71}BM$/LiF (1 nm)/Al (100 nm). The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water and acetone. The poly(ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) layer was spin-coated on the substrate and annealed at 120°C for 20 min. The active layer was prepared by spin-coating a chlorobenzene solution containing oligomer and $PC_{71}BM$ at 1500 rpm on the ITO/PEDOT:PSS electrode. Finally, LiF/Al layers were thermally deposited as the cathode electrode. The area of the device was 4 mm^2. After annealed at 100°C for 10 min, the current-density versus voltage ($J-V$) characteristics of the oligomer:$PC_{71}BM$ films were measured with a Keithley 2400 source-measure unit in air under white illumination of AM 1.5G (100 mW/cm^2).

Results and Discussion

Synthesis and Physical Properties

The oligothiophene, ***β*-DH5T** was synthesized via the palladium-catalyzed Suzuki coupling [13] between a dibromoaryl compound of 5,5"-dibromo-2,2':5',2"-terthiophene (**1**) and a diborolanylaryl compound of 4-hexyl-2-thiopheneboronic acid pinacol ester. The synthetic route and chemical structure of the oligomer are shown in Scheme 1. ***β*-DH5T** features the conjugated backbone of quinquethiophene (5T) with solubilizing *β*-substituted hexyl side chains at both ends. ***β*-DH5T** was readily soluble in common organic solvents such as



Scheme 1. Synthetic procedure of oligomer. (i) NBS, DMF at 0°C, then room temperature for 2h; (ii) $Pd(PPh_3)_4$, Na_2CO_3 (*aq*, 2M), toluene, Aliquat®336, 95°C, N_2 for 3 days.

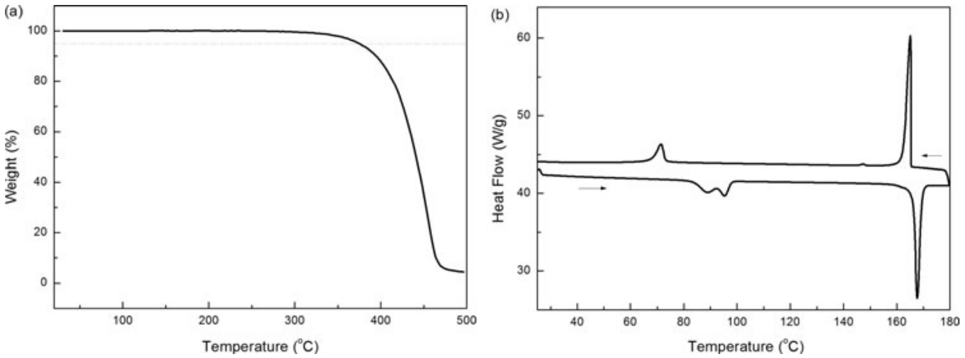


Figure 1. (a) TGA and (b) DSC thermograms of β-DH5T.

chloroform and chlorobenzene, making it a good candidate for solution-processed OPVs. The synthesized oligomer was successfully characterized by ^{1}H and ^{13}C NMR, spectroscopy and elemental analysis. The thermal behavior of the oligothiophene was determined using DSC and TGA as shown in Figure 1. The melting peak of β-**DH5T** occurred at 168°C with a recrystallization peak at 165°C. The decomposition temperature (T_{5d}) that resulted in 5% weight loss based on the initial weight of β-**DH5T** was 375°C, indicating that β-**DH5T** was sufficiently thermally stable for use in OPV applications.

The optical and electrochemical properties of β-**DH5T** are shown in Figure 2 and the optical properties are listed in Table 1. Figure 2a shows normalized UV-vis absorption and photoluminescence (PL) emission spectra of β-**DH5T** in a dilute chlorobenzene solution and as a film. The absorption spectrum of β-**DH5T** features a single peak with a maximum at around 420 nm. The absorption spectrum of the β-**DH5T** film ($\lambda_{\max} = 340$ nm) in the solid state was blue-shifted compared to that in solution. Similar behavior was reported for other oligothiophene films, in which the closed-packed arrangement of the molecules led to splitting of the excited state into two exciton states (i.e., Davydov splitting). The blue shift from the solution to the film states indicated the presence of strong interactions among the π-conjugated systems in the film state, suggesting the formation of an *H*-aggregate–type structure[9,14,15]. Additionally, the spectrum of the β-**DH5T** film exhibited a long tail extending up to 800 nm; this broad UV absorption in the long wavelength region could lead

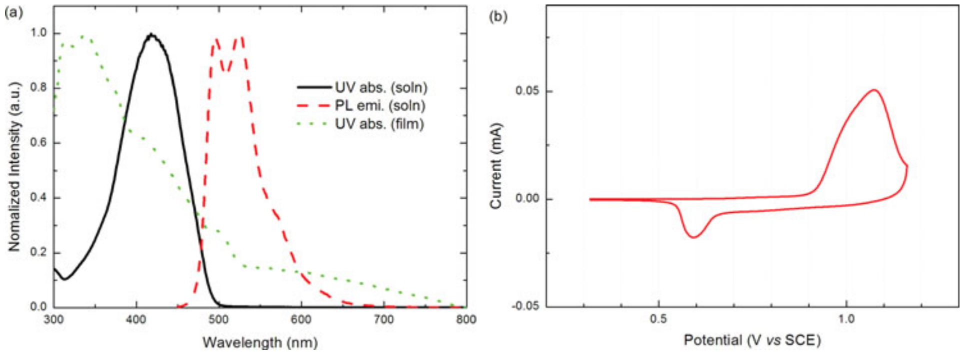


Figure 2. (a) UV–visible absorption and PL emission spectra in chlorobenzene solution and in film and (b) CV of β-DH5T.

Table 1. Physical and optical properties of oligomer (β-DH5T)

T_{5d}	UV λ_{max} (nm)		p-doping (V vs SCE)^a				E_{HOMO}	E_{LUMO}	E_g
(°C)	Solution	Film	E_{pa}	E_{pc}	$E_{1/2}$	E_{onset}	(eV)	(eV)	(eV)
375	420	340, 416, 500	1.07	0.59	0.83	0.91	–5.31	–2.95	2.36

[a] E_{pa}, E_{pc}, $E_{1/2}$, and E_{onset} stand for anodic peak potential, cathodic peak potential, the average of the anodic and cathodic peak potentials, and onset potential of oxidation, respectively.

to improved OPV performance because of better overlap with the solar spectrum[16]. The optical band gap (E_g) of the β-**DH5T**, as estimated from the absorption onset wavelength of the oligomer film ($E_g = 1240/\lambda_{onset}$ eV), was 2.36 eV. The electrochemical properties of the oligomers were characterized by CV (Figure 2b and **Table 1**). The HOMO level and the lowest occupied molecular orbital (LUMO) levels of β-**DH5T** were –5.31 eV and –2.59 eV, respectively.

Charge-Transport Properties and Organic Photovoltaic Properties

An XRD study was performed to investigate the molecular orientation and charge-transport properties of the synthesized oligothiophene. XRD patterns of the β-**DH5T** film are shown in Figure 3 together with that of the β-**DH5T:**PC$_{71}$BM blend film. The pristine β-**DH5T** film showed a series of multiple (h00) reflections at $2\theta = 2.49$, 5.07, and 7.66°, which were assigned to (100), (200), and (300) reflections, respectively. The first strong (100) reflection peak at $2\theta = 2.49°$, which was indicative of a d spacing of 35.45 Å, was very similar to that of the α-**DH5T** film, which showed a first strong reflection peak at $2\theta = 2.58°$ ($d = 34.2$ Å[12]. Therefore, similar to well-known α-substituted α-**DH5T**, a well-defined edge-on orientation relative to the substrate might be maintained in the β-**DH5T** film, which could enhance the transport properties by maximizing the π–π overlap between adjacent molecules[9]. It is worth noting that the reflections evident in the XRD pattern of

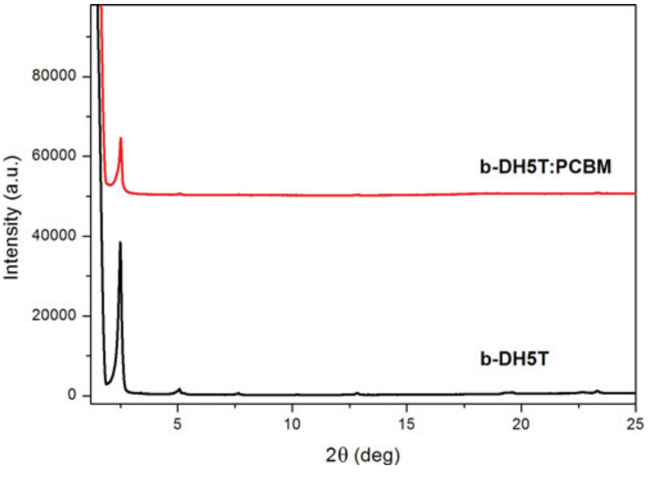


Figure 3. XRD patterns of the pristine β-DH5T film together with β-DH5T:PC$_{71}$BM blend film.

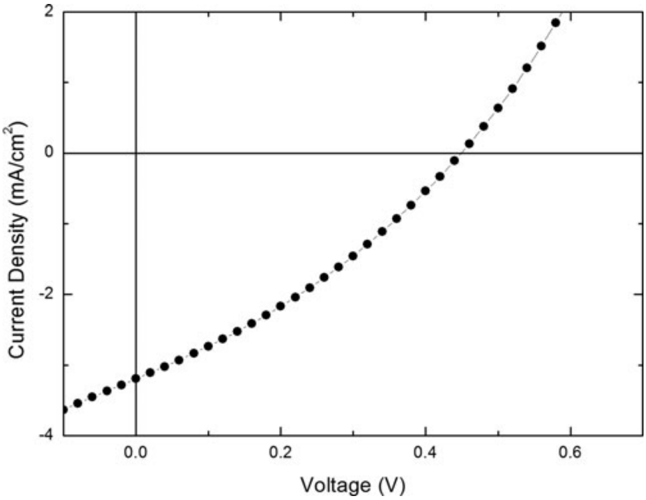


Figure 4. *J–V* curves for the photovoltaic cells of β-DH5T:PC$_{71}$BM film.

the β-**DH5T** film were also observed in the pattern of the β-**DH5T** and PC$_{71}$BM blend film. Therefore, we expect that the good molecular packing of the β-**DH5T** film was somewhat maintained in the blend film of OPV devices.

OPV devices were fabricated with the following configuration: ITO/PEDOT:PSS/oligomer:PC$_{71}$BM/LiF/Al. The oligomer and PC$_{71}$BM blend solutions were spin-coated onto PEDOT:PSS-coated ITO substrates to form a bulk-heterojunction active layer. After annealing at 100°C for 10 min, the current–density versus voltage (*J–V*) characteristics of the oligomer:PC$_{71}$BM blend films were measured in air. Figure 4 shows the *J–V* curves measured in air under white AM 1.5G illumination (100 mW/cm^2). Owing to the good solubility, β-**DH5T** could be used as a donor material in solution-processed OPV devices. The β-**DH5T**:PC$_{71}$BM film showed a moderate power conversion efficiency (PCE) of 0.46% with an open-circuit voltage (V_{OC}) of 0.45 V, a short-circuit current (J_{SC}) of 3.19 mA/cm^2, and a FF of 0.32. Despite the good molecular packing of the β-**DH5T** film as evident from the XRD and UV-vis spectroscopy results, the photovoltaic performance of β-**DH5T** was relatively poor compared to those of other donor–acceptor (D−A) type polymer-based photovoltaic cells. The low efficiency of β-**DH5T** was likely caused by its relatively large energy band gap of 2.36 eV. Therefore, the J_{SC} value could be improved by introducing electron-accepting moieties such as benzothiadiazole and diketopyrrolopyrrole into the molecular backbone. Here, we demonstrated a simple strategy to improve the solubility of the material for solution-processed OPV cells. Improvement of the photovoltaic performance by modifying the molecular structure and/or optimizing the of fabrication conditions will be studied in the future.

Conclusions

We synthesized the solution-processable small molecule based on quinquethiophene by introducing β-substituted alkyl groups. Proper β-substitution of the alkyl groups resulted in good molecular packing of the rod-like oligothiophenes and improved material solubility. Here, β-**DH5T** yielded an optimized OPV performance of 0.46% in a solution-processed OPV device.

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