

Synthesis of 4,8-dialkoxy-benzo[1,2-b:4,5-b']difuran unit and its application in photovoltaic polymer

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Characterization

¹H and ¹³C NMR spectra were measured on a Bruker DMX-400 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. The molecular weight of polymers was measured by GPC method, using polystyrene as a standard. TGA was performed on a PE TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk coated with the polymer film, Pt wire, and Ag/Ag⁺ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution.

Materials

Furan-3-carbonyl chloride, 1. In a 50 mL round flask, oxalyl chloride (40 mL) was dropped into a furan-3-carboxylic acid (5.0 g, 44.6 mmol) solution in 25 mL methylene chloride at room temperature and the reaction was kept for 12h at the same temperature. Then the mixture was evaporated by rotary evaporation to remove the solvent and oxalyl chloride. The residue was obtained as light yellow liquid and used directly without further purification.

N,N-diethylfuran-3-carboxamide, 2. Compound 1 (5.8 g, 44.6 mmol) was dissolved in methylene chloride (20 mL) then the solution was dropped into a diethylamine (10 mL) solution in methylene chloride (30 mL) slowly in ice-water bath. After adding compound 1, the mixture was warmed up to room temperature and stirred for another 40 minutes. Then, the mixture was washed by water and extracted by methylene chloride. The combined organic phase was dried over

anhydrous MgSO_4 and evaporated by vacuum to remove the solvent. The residue was purified by distillation under vacuum to obtain compound 2 as pale yellow oil (6.3g, yield: 85%). ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.71(s, 1H), 7.42 (s, 1H), 6.59 (s, 1H), 3.49 (q, 4H), 1.21 (t, 6H).

Benzo[1,2-b:4,5-b']difuran-4,8-dione, 3. Compound 2 (28.47 g, 0.17 mol) was dissolved in anhydrous tetrahydrofuran (150 mL); then n-butyl lithium (75 mL, 2.5 M) was dropped into the solution in 20 minutes at 0 °C. Then, the cooling bath was removed and the mixture was warmed up to room temperature and stirred overnight. After 15 hours, a dilute hydrochloric acid (100 mL, 3mol/L) was added to quench the reaction. Then the mixture was washed twice by water and extracted by methylene chloride five times. The combined organic phase was combined and evaporated by vacuum to remove the solvent. The solid residue was recrystallized from dichloromethane to get the pale yellow crude product. (11.0 g, yield: 69%). Further purification could be carried out from several recrystallizations in dichloromethane. ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.71(s, 2H), 6.92 (s, 2H). [melting point: 137°C](#).

4,8-bis(2-ethylhexyloxy)benzo[1,2-b;3,4-b]difuran, 4. Compound 3 (2.05 g, 11 mmol) was suspended into ethanol (50 mL) in a ice-water bath, then sodium borohydride (1.1 g, 27.3 mmol) was added into the solution and stirred at 0°C. After 3h, a solution of hydrochloric acid (50 mL, 2 mol/L) was added to the mixture to quench the reaction. The mixture was filtered and the solid was washed twice by water and dried in vacuum to get solid powder. Then the powder and potassium carbonate (3.04 g, 22 mmol) were mixed in DMF (50 mL). Under inert atmosphere, 2-ethylhexyl bromide (8.5 g, 44 mmol) was injected by a syringe and the mixture was stirred for another 15h at 150 °C. Then, the reactant was poured into cool water and extracted by methylene chloride. The combined organic phase was dried over anhydrous MgSO_4 and evaporated by vacuum to remove the solvent. The residue was purified column chromatography on silicon gel using hexane as eluent. The compound 4 was obtained as colorless oil. (2.4g, yield: 52%) ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.53(s, 2H), 6.92 (s, 2H), 4.33 (d, 4H), 1.81(m,2H), 1.57-1.31 (m, 16H), 0.95 (m, 12H). ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): [144.04, 142.42, 131.30, 119.36, 104.73, 75.58, 40.25, 30.42, 29.13, 23.78, 23.15, 14.15, 11.17](#).

2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b;3,4-b]difuran, BDF. Under inert atmosphere, n-butyl lithium (1.2 mL, 2.5 M) was injected into the solution of compound 4 (0.208 g, 0.5 mmol) in THF (20 mL) at room temperature and the mixture was stirred for 1 hour. Then chloro-trimethylstannane (3.5 mL, 1 M in hexane) was added and stirred for another 0.5h. The mixture was poured into water and extracted by diethyl ether. The combined organic phase was dried over anhydrous MgSO_4 and evaporated by vacuum to remove the solvent. The product was obtained as pale yellow oil and used without further purifications. (0.34g, yield: 92%). ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.11(s, 2H), 4.41 (d, 4H), 1.76(m,2H), 1.54-1.38 (m, 16H), 0.98 (m, 12H), 0.48 (s, 18H); ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): δ 164.20, 146.18, 129.97, 120.03, 115.43, 75.36, 40.22, 30.56, 29.19, 23.89, 23.25, 14.26, 11.25, -9.09.

Poly{4,8-bis(2-ethylhexyloxy)benzo[1,2-b;3,4-b']difuran-alt-2,6-diyl-alt-[4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-2,1,3-benzothiadiazole]-5,5'-diyl} PBDFDTBT.

The monomer of BDF (0.5mmol) and the dibromo-monomer of DTBT (0.5 mmol) were mixed in 10 ml of toluene. After being purged by argon for 5 min, 25 mg of $\text{Pd}(\text{PPh}_3)_4$ was added as catalyst, and then the mixture was purged by argon for 25 min. The reactant was stirred and heated to reflux for 16 hours under inert atmosphere. Then the reactant was cooled down to room temperature, and the polymer was precipitated by addition of 50 ml methanol, and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction. The solid was dried under vacuum. The yield and elemental analytical results of the polymers are as follows

Yield: 40%. Molecular weight: $M_w=10.4\text{K}$, $\text{PDI}=1.62$. Elemental analysis: calculated as $\text{C}_{56}\text{H}_{74}\text{N}_2\text{O}_4\text{S}_3$, C, 71.91; H, 7.97; N, 2.99; found: C, 71.62; H, 7.94; N, 2.95.

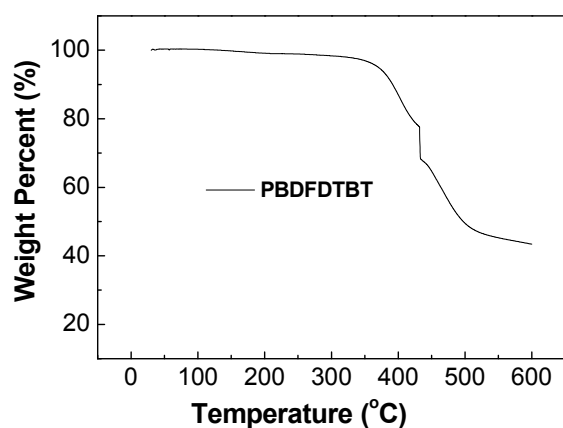


Fig. s1 TGA plot of PBDFDTBT with a heating rate of 10 °C /min in the inert atmosphere.

Fabrication of polymer solar cell devices. polymer solar cell devices with the structure of ITO/PEDOT-PSS/polymer:PCBM₇₀/Ca/Al were fabricated under conditions as follows: After spin-coating a 30-50 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a pre-cleaned indium-tin oxide (ITO) coated glass substrate, the polymer/PC₇₀BM blend solution was spin-coated. The concentration of the polymer/PCBM₇₀ (1:0.5, 1:0.8, 1:1, 1:1.5 and 1:2, weight ratio) blend solutions used in this work for spin-coating active layer was 10 mg/ml (according to the polymer weight), and dichlorobenzene was used as solvent. 3% (v/v) DIO was used as additive, or pre-thermal annealing was used to improve photovoltaic performance of the devices. The thickness of the active layer was ~90 nm. The devices were completed by evaporating Ca/Al metal electrodes with area of 0.1 cm² defined by masks. Testing was done in N₂ under simulated AM1.5G irradiation (100 mW/cm²) using a xenon-lamp-based solar simulator with an AM 1.5G filter (obtained from Newport Corporation).

Hole mobility measurement and fabrication of polymer solar cells. We used a device structure of ITO/PEDOT:PSS/polymer:PC₇₀BM/Au for the hole mobility measurement, based on the space-charge-limited current (SCLC) model.

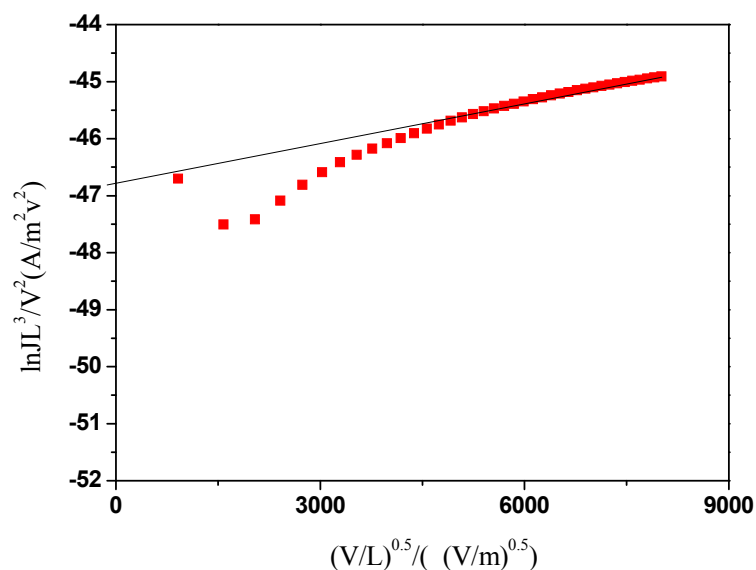


Fig. s2 SCLC mobility model measure plot of PBDFDTBT.

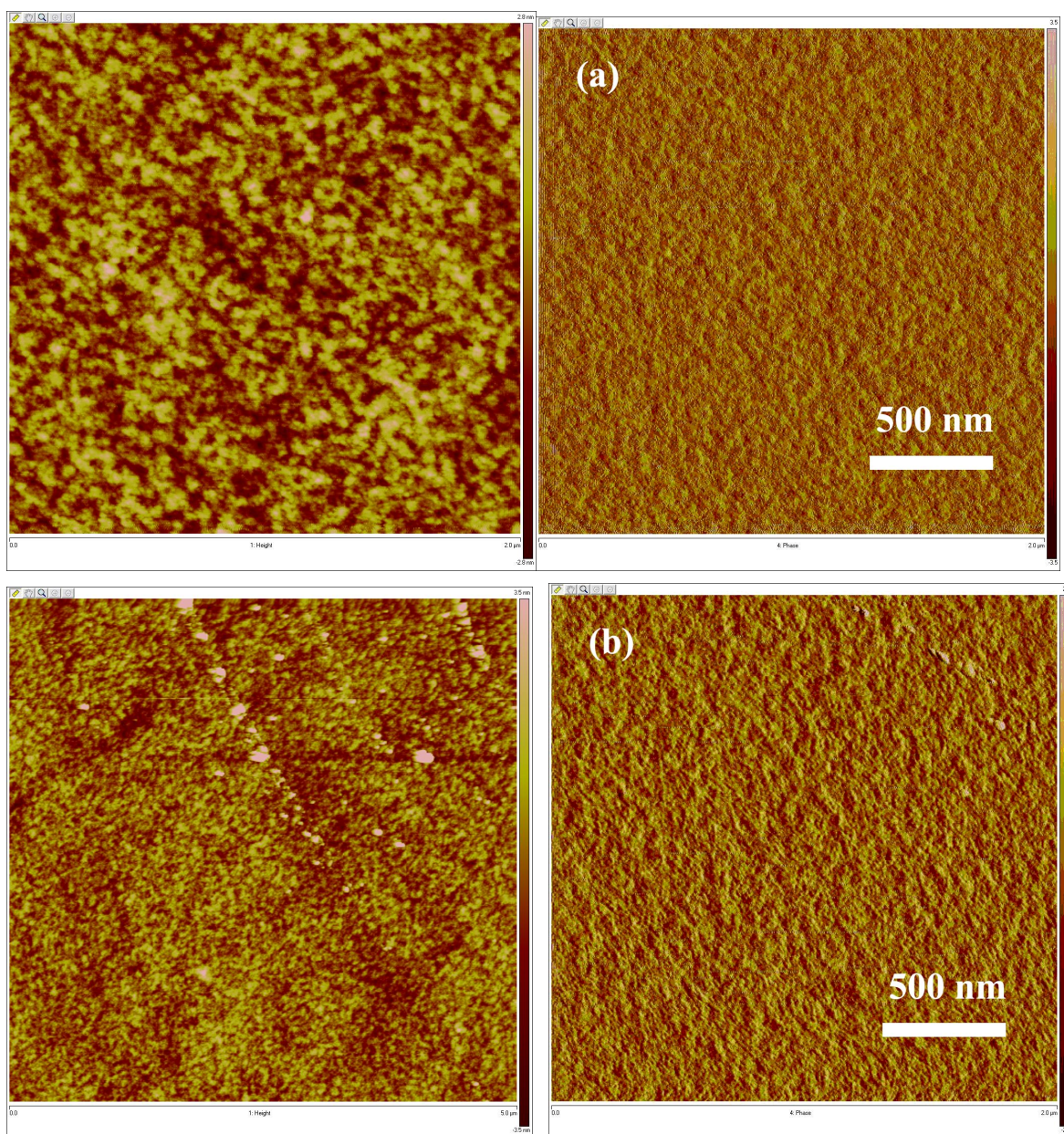


Fig. s3 AFM images ($2 \times 2 \mu\text{m}^2$) of the active layers from PBDFTBT:PC₇₀BM with weight ratio: (a) 1:1.5; (b) 1:1.5, annealed.