

Anionic Benzothiadiazole Containing Polyfluorene and Oligofluorene as Organic Sensitizers for Dye-sensitized Solar Cells

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Supporting Information

Materials

2-Bromofluorene, *t*-butyl acrylate and bis(pinacolato)diboron was purchased from Aldrich. The monomer 4,7-dibromo-2,1,3-benzothiadiazole (**3**) were synthesized according to the previous literatures.¹ Other chemicals and reagents were used as received from Aldrich or Acros without further purification.

Instrumentation

The photocurrent-photovoltage measurements were recorded by the electrochemical workstation (PGSTAT30, Autolab). A Xe lamp (Model 66902, Oriel) with an AM 1.5 light filter was used as the white light source for measuring the solar cells. The intensity of incident light was calibrated with a radiometer (Model 8-48, Eppley) before each experiment. Incident photon to collected electron efficiency (IPCE) was measured using a 200 W Xe lamp light source with a motorized monochromator (Oriel).

The ¹H NMR and ¹³C NMR spectra were taken on a Bruker 300 MHz spectrometer. UV-Vis absorption spectra were collected with a Shimadzu UV-1700 spectrophotometer. GPC analysis was conducted at 35 °C using a Waters 2690 liquid

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chromatography system equipped with a Waters 996 photodiode detector. Polystyrenes were used as the standard and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. Cyclic voltammetry was carried out on a computer-controlled PGSTAT30 electrochemical workstation (Autolab) with a glass carbon electrode as the working electrode, a platinum wire electrode as the counter electrode and Ag/AgCl as a reference electrode. The scan rate is 100 mV/s. 0.1 M tetrabutylammonium hexafluorophosphate in DMF was used as the electrolyte.

Synthesis

2-Bromo-9,9-bis(3-(t-butyl propanoate))fluorene (1)

50 wt% aq NaOH (5 mL) was added dropwise into a solution of 2-bromofluorene (3.03 g, 12.4 mmol) and tetrabutylammonium bromide (105 mg, 0.33 mmol) in toluene (20 mL). The solution was stirred for 20 min at room temperature. t-Butyl acrylate (6.56 g, 51.2 mmol) was added dropwise and the mixture was stirred at room temperature for 5 hours. The mixture was diluted with dichloromethane (15 mL) and washed with water (10 mL × 2). The organic layer was dried over anhydrous MgSO₄. After removing the solvent, the residue was purified by column chromatography (dichloromethane : hexane = 1 : 1) to give **1** (4.1 g, 66 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.70-7.32 (m, 7H), 2.30 (q, J = 6.0 Hz, 4H), 1.43 (t, J = 8.4 Hz, 4H), 1.30 (s, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 172.5, 150.3, 147.7, 140.0, 130.7, 128.1, 127.7, 126.4, 123.1, 121.5, 120.0, 119.9, 80.2, 53.8, 34.5, 29.9, 28.0. MALDI-TOF for C₂₇H₃₃BrO₄, 500.99 (M).

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(3-(t-butyl propanoate))fluorene (2)

A mixture of **1** (3.27 g, 6.5 mmol), KOAc (2.7 g, 27.5 mmol) and bis(pinacolato)diboron (4.2 g, 16.5 mmol) in DMF (40 mL) was placed in a 100 mL flask. After stirring for 10 min, Pd(dppf)₂Cl₂ (150 mg) was added quickly. The mixture was stirred overnight at 90 °C. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane (15 mL × 2). The organic layer was washed with water (10 mL × 2) and then dried over anhydrous MgSO₄. After removing the solvent, the residue was purified by column chromatography (ethyl acetate : hexane = 1 : 4) to give **2** (2.4 g, 56 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.83-7.68 (m, 4H), 7.38-7.33 (m, 3H), 2.36 (m, 4H), 1.40 (m, 4H), 1.37 (s, 12H), 1.29 (s, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 173.2, 149.1, 147.7, 144.4, 141.4, 134.8, 129.4, 128.5, 127.9, 123.5, 120.8, 119.6, 84.2, 80.4, 53.9, 35.0, 30.4, 28.4, 25.4. MALDI-TOF for C₃₃H₄₅BO₆ 548.19 (M).

4,7-Bis(9,9-bis(3-(t-butyl propanoate))fluoren-2-yl)-2,1,3-benzothiadiazole (4)

Monomer **2** (700 mg, 1.28 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (180 mg, 0.61 mmol) were added into a 50 mL two-neck flask. K₂CO₃ (560 mg), Pd(PPh₃)₄ (10 mg), toluene (10 mL) and water (3 mL) were then added. After degassing, the mixture was heated at 90 °C with vigorous stirring for 24 hours. After the mixture was cooled down to room temperature, toluene was evaporated. The residue was extracted with CH₂Cl₂, and washed twice with water. The organic layer was collected and dried with MgSO₄. After filtration, CH₂Cl₂ was evaporated and the residue was purified with silica chromatography using CH₂Cl₂/Hexane (v/v = 3:2) to yield **4** (380 mg, 70%) as light yellow solids. ¹H NMR (300 MHz, CDCl₃): δ 8.15-7.77 (m, 10H), 7.44-7.37 (m, 6H), 2.54 (m, 8H), 1.64 (m, 8H) 1.30 (s, 36H). ¹³C NMR (75 MHz, CDCl₃): δ 173.2, 154.6,

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149.1, 148.9, 141.8, 141.2, 137.1, 134.8, 133.7, 129.4, 128.4, 128.0, 124.3, 123.6, 120.7, 120.4, 80.4, 54.1, 35.1, 30.6, 28.4. MALDI-TOF for C₆₀H₆₈N₂O₈S 976.38 (M).

4,7-Bis(9,9-bis(3"-propanoic))fluoren-2-yl)-2,1,3-benzothiadiazole (DFBT)

In a 50 mL flask, compound **4** (50 mg) was dissolved in CH₂Cl₂ (25 mL). After addition of trifluoroacetic acid (2 mL), the mixture was stirred overnight at room temperature. After removal of the solvent, the yellow-greenish residue was extracted with CH₂Cl₂, and washed twice with water. The organic layer was collected and dried with MgSO₄. The solvent was filtered and evaporated and the product was vacuum-dried for 12 h to yield **DFBT** as a greenish yellow solid. ¹H NMR (300 MHz, CD₃OD): δ 7.94-7.82 (m, 6H), 2.61 (br, 4H), 1.65 (br, 4H). MALDI-TOF for C₄₄H₃₆N₂O₈S 752.16 (M).

Poly[9, 9-bis(3'-(t-butyl propanoate))fluorene-co-4,7-(2,1,3-benzothiadiazole)₃₀] (7)

Monomer **3** (88 mg, 0.30 mmol), monomer **5** (116 mg, 0.20 mmol), monomer **6** (337 mg, 0.50 mmol), Pd(PPh₃)₄ (8 mg) and potassium carbonate (830 mg, 6 mmol) were placed in a 25 mL round bottom flask. A mixture of water (3 mL) and toluene (9 mL) was added to the flask and the reaction vessel was degassed. The mixture was heated at 90 °C for 24 hours under argon, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum overnight to afford the neutral polymer **7** (220 mg, 65%) as a yellow fibrous solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.17 (br, 0.60H), 7.72-8.02 (br, 6H), 2.55 (br, 4H), 1.75 (br, 4H), 1.31 (s, 18H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 173.24, 154.68, 149.63, 141.36, 137.43, 133.76, 132.50, 129.62, 128.56, 124.49, 120.73, 80.50, 54.45, 35.08, 30.77.

Poly[9, 9-bis(3'-propanoic acid)fluorene-co-4,7-(2,1,3-benzothiadiazole)₃₀] (PFBT).

Polymer 7 (100 mg) was dissolved in dichloromethane (25 mL) in a 50 mL flask. After addition of trifluoroacetic acid (3 mL), the mixture was stirred for 4 hours at room temperature. After removal of the solvent, the yellow-greenish residue was extracted with dichloromethane, and washed with water twice. The organic layer was collected and dried with MgSO₄. The solvent was filtered and evaporated and the product was vacuum-dried for 12 h to yield **PFBT** (80 mg, 93%) as an orange solid. ¹H NMR (300 MHz, CD₃OD) δ (ppm): 8.22 (m, 0.59H), 7.89-8.00 (m, 6H), 2.60 (br, 4H), 1.58 (br, 4H).

Table 1. Optical and electrochemical data of PFBT and DFBT and their performance in DSSC.

Dye	$\lambda_{\text{abs}}^{\text{a}}$ / nm	E_{ox}^{b} / V	E_{0-0}^{c} / eV	($E_{\text{ox}} - E_{0-0}$) / V	$I_{\text{sc}} / \text{mA cm}^{-2}$	$V_{\text{oc}} / \text{mV}$	FF	η^{d} (%)
PFBT	444	1.25	2.44	-1.19	4.03	523	0.66	1.39
DFBT	420	1.34	2.53	-1.19	3.47	459	0.66	1.05

^aAbsorption spectra were measured in DMF solution at 1.6×10^{-2} mg/mL. ^bThe ground state oxidation potential was measured by CV method, using glassy carbon as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. ^c E_{0-0} was estimated from the onset of the absorption spectra. ^dThe photocurrent density-voltage data were measured under 100mW/cm² AM1.5 illumination.

Reference

- (1) Liu, B.; Bazan, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1942.