



A unique concept of copolymer composed of main chain donor and side chain acceptor for promising bulk heterojunction solar cells



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ABSTRACT

An alternating copolymer of thiophene and thienothiophene with a cyanoacrylate group conjugated side chain was designed and synthesized. The structure and property of the main chain donor-side chain acceptor orthogonal copolymer was fully characterized. Through this unique structure of a copolymer, the electronic property and light absorption range were effectively tuned. The structure characteristics of an orthogonally conjugated polymer were also studied by molecular simulation. The polymer was used as donor in polymer solar cells. The device based on CNTT/PC₇₁BM demonstrates a power conversion efficiency of 1.21% with a high J_{SC} of 6.51 mA cm⁻² under the illumination of AM 15.G, 100 mW cm⁻².

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1. Introduction

Developing organic solar cells (OSCs) continues to raise research interests due to several distinct advantages, such as mechanical properties and high-throughput yet low-cost processing [1–4]. In particular, bulk heterojunction OSCs based on a semiconducting polymer blended with a fullerene derivative are making significant advances in efficiency and provide the prospect of a viable renewable energy source in the future [5–6]. The operation of these solar cells relies on the efficient photo-induced electron transfer reaction between the semiconducting polymer as electron donor and the fullerene as electron acceptor [7–8]. The alternation of electron-rich and electron-deficient π -conjugated moieties has proven to be a very successful strategy in intramolecular charge-transfer characteristics and wide absorption bands [9–11]. Most systems in polymer materials class employ a structural motif where the electron donor and electron acceptor units are linked in a linear fashion, *i.e.*, -D-A-D-A-D-A-. Recently, orthogonally conjugated structures – where the electron acceptor (or donor) is appended to the side of the main, conjugated

backbone – have been introduced as an alternative strategy [12–13]. For instance, Zhang et al. showed that manipulating the electron-withdrawing strength of the acceptor groups attached to a backbone consisting of carbazole and thiophene units, allowed the redox and optical properties to be effectively tuned [14]. In addition, Grimm et al. also exhibited a copolymer comprised of cyclopentadithiophene (CPDT) with an imine functionality appended to the CPDT bridgehead position containing mainly low-energy absorption characteristics [15]. Despite their remarkable polymeric structure, there are relatively few examples of orthogonal conjugated polymers.

Herein, therefore, we report the synthesis and characterization of an orthogonal conjugated copolymer incorporating the main chain donor-side chain acceptor architecture. We focus on thiophene and thienothiophene as suitable electron rich comonomers. Thiophene and thienothiophene have been utilized in various high performing conjugated copolymers, and they generally promote high hole mobility with its simple and rigid structure and good photocurrent [16]. As an electron-deficient group, we investigated the cyano acrylate unit due to the superior electron-withdrawing properties and promising performance of the alternating copolymer with the cyano group, which was previously reported [17–18]. We find that our orthogonal conjugated polymer by the copolymerization of thiophene and thienothiophene in the main chain with the cyano acrylate group

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substituent as a side-chain acceptor has a beneficial impact on the light absorption range of the strongly near infrared region of 1000 nm. Also, good processability and an uncompromised photovoltaic performance were achieved by using this polymer as the donor material of in BHJ solar cells.

2. Experimental

2.1. Materials

All chemical reagents were purchased from Aldrich and used as received without further purification. Solvents were properly dried or distilled before use in the syntheses and spectroscopic studies.

2.2. Synthesis

2.2.1. 4-Bromothiophene-3-carbaldehyde

3,4-Dibromo thiophene (50 g, 0.20 mol) was dissolved in anhydrous diethyl ether (500 mL), and *n*-BuLi (83 mL, 0.20 mol) dropwise added in the mixture at -78°C under nitrogen atmosphere. After the reaction mixture stirred for 30 min, *N,N*-dimethylformamide was slowly added to the mixture, and then stirred at -78°C for 3 h. After the reaction mixture was poured into water and extracted with diethyl ether. The combined organic layers were dried over MgSO_4 , and the solvent removed by rotary evaporation. The reaction mixture was purified by distillation. Yield: 30 g (78.51%), bp: $80\text{--}90^{\circ}\text{C}/4$ torr; $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 9.95 (s, 1H), 8.16 (d, 1H), 7.37 (d, 1H).

2.2.2. Ethyl thieno[3,4-*b*]thiophene-2-carboxylate

4-Bromothiophene-3-carbaldehyde (30 g, 0.157 mol), ethyl 2-sulanyl acetate (20.73 g, 0.172 mol), copper oxide nanopowder (2.49 g, 0.0314 mol) and K_2CO_3 (28.21 g, 0.204 mol) were dissolved in dimethylsulfoxide. The reaction mixture was heated at 80°C in the nitrogen during for 12 h, and then the mixture was poured ice water and extracted with ether. The combined organic layers were dried over MgSO_4 , and the solvent removed by rotary evaporation and the desired product was purified by column on silica-gel (hexane using as eluent) to give a yellow solid. Yield: 26.33 g (79%), mp: $200\text{--}220^{\circ}\text{C}$, $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.72 (s, 1H), 7.76 (d, 1H), 7.31 (d, 1H) 4.43 (q, 2H), 1.43 (t, 3H).

2.2.3. Thieno[3,4-*b*]thiophene-2-ylmethanol

Thieno[3,4-*b*]thiophene-2-carboxylate (26 g, 0.122 mol) was dissolved in anhydrous ether (300 mL), and LiAlH_4 (2.67 g, 0.122 mol) was added in the mixture several times. The reaction mixture was stirred for 30 min. After the reaction mixture was poured to 1 M NaOH organic layer was extracted with diethyl ether. The combined organic layer was dried over MgSO_4 , and the crude product was purified by column on silica-gel using hexane:ethyl acetate 7:3 as eluent to give a yellow solid. Yield: 19.01 g (91.2%), mp: $221\text{--}222^{\circ}\text{C}$; $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.26 (d, 1H), 7.21 (d, 1H), 6.81 (s, 1H), 4.75 (s, 2H), 2.39 (s, 1H (—OH)).

2.2.4. Thieno[3,4-*b*]thiophene-2-carbaldehyde

PCC (pyridinium chlorochromate) (28.86 g, 0.133 mol) was slowly added to a mixture of thieno[3,4-*b*]thiophene-2-ylmethanol (19 g, 0.111 mol) in methyl chloride at room temperature in the nitrogen during overnight, and then the mixture was poured into water and the organic layer was extracted with diethyl ether. The combined organic layer was dried over MgSO_4 , and the solvent removed by rotary evaporation. Yield: 14.56 g (78.12%), bp: $120\text{--}125^{\circ}\text{C}/0.1$ mmHg; $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 10.01 (s, 1H), 7.78 (d, 1H), 7.69 (s, 1H), 7.35 (d, 1H).

2.2.5. 4,6-Dibromothieno[3,2-*c*]thiophene-2-carbaldehyde

Thieno[3,4-*b*]thiophene-2-carbaldehyde (5 g, 0.029 mol) and AcOH (25 mL). *N*-bromosuccinimide (11.57 g, 0.065 mol) in CHCl_3 (25 mL) and AcOH (25 mL) were added at 0°C in the nitrogen during 30 min. After reaction, the mixture was stirred at room temperature in the nitrogen during overnight, the organic layer of the mixture was poured water and extracted with CHCl_3 . The combined organic layer was dried over MgSO_4 , and the solvent was removed by rotary evaporation, and the desired product was purified by column on silica gel using hexane:ethyl acetate 10:1 as eluent to give a yellow solid. Yield: 6.8 g (70%), $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 9.99 (s, 1H), 7.86 (s, 1H).

2.2.6. 2-Octyldodecyl 2-cyanoacetate

Cyan acetic acid (7.6, 0.089 mol) and 2-octyl-dodecan-1-ol (22.27 g, 0.074 mol) in 200 mL of toluene were added H_2SO_4 (0.4 mL). The solution was refluxed for 16 h at 100°C in the nitrogen atmosphere. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica-gel) using hexane/ethyl acetate (5:1) to afford 13.23 g (49%), $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 3.57 (s, 2H), 2.41 (t, 2H), 1.70 (t, 1H), 1.33–1.25 (m, 32H), 0.96 (d, 6H).

2.2.6.1. (*Z*)-2-octyldodecyl-2-cyano-3-(4,6-dibromothieno[3,4-*b*]thiophene-2-yl) acrylate (A). The piperidine (0.28 g, 3.37 mmol) was added to a mixture of 4,6-dibromothieno[3,2-*c*]thiophene-2-carbaldehyde (1 g, 3.06 mmol) and 2-octyldodecyl 2-cyanoacetate (1.68 g, 4.60 mmol) in ethanol (2 mL) and CH_3CN (20 mL). The reaction mixture was refluxed for 3 h. The mixture was poured into water and extracted with chloroform. The combined organic layers were dried with over MgSO_4 , and the solvent removed by rotary evaporation. And the desired product was purified by column (hexane:ethyl acetate 10:1 as eluent) to give a product. Yield: 1.05 g (51.2%), $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.42 (s, 1H), 7.20 (s, 1H), 3.08 (t, 2H), 1.82 (t, 1H), 1.28 (m, 32H), 0.90 (t, 6H), FT-IR (KBr) (cm^{-1}) 3010 (aromatic), 2860–2780 (aliphatic, C—H), 2230–2252 (CN), 1700–1680 (carbonyl, C=O), 809 (aliphatic, C—S).

2.2.7. 2,5-Bis-trimethylstannanyl-thiophene

n-BuLi (50 mL, 125 mmol) was added to a stirring solution of thiophene (5 g, 59.5 mmol) in anhydrous THF at -78°C under nitrogen atmosphere. The reaction mixture was stirred at 0°C for 1 h. After the mixture was dropwise added SnMe_3Cl (24.87 g, 125 mmol) at -78°C under nitrogen atmosphere, and then reaction mixture was stirred at room temperature for 4 h. And then the mixture was poured into water and the organic layer was extracted with diethyl ether. The combined organic layer was dried over MgSO_4 , and the solvent removed by rotary evaporation. And the desired product was purified by column on silica-gel using hexane as eluent to give a product. Yield: 19.9 g (82%), $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): 7.10 (d, 2H), 0.39 (s, 18H).

2.2.7.1. Poly[*Z*]-2-octyldodecyl-2-cyano-3-(6-thiophene-2-yl)thieno[3,4-*b*]thiophene-(2-yl)acrylate. 2,5-Bis-trimethylstannanyl-thiophene (0.303 g, 0.74 mmol) was added to a mixture of 2-octyldodecyl-2-cyano-3-(4,6-dibromothieno[3,4-*b*]thiophene-2-yl) acrylate (0.5 g, 0.74 mmol) in chlorobenzene (7 mL) under nitrogen atmosphere for 30 min. After $\text{Pd}_2(\text{dba})_3$ (0.01355 g, 0.00148 mmol) and $\text{P}(o\text{-tol})_3$ (0.1018 g, 0.00592 mmol) were added into the reaction mixture, the reaction mixture was refluxed at 90°C for 72 h. In the reaction mixture, 2-bromobenzene and tributyl(phenyl)stannane were added and refluxed for 12 h. The crude product was dissolved in chloroform and precipitated into methanol. Then the polymer was filtered. The polymer was purified by soxhlet with methanol acetone, hexane

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