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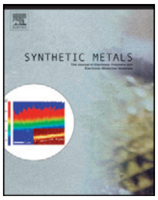

Syntheses and properties of cyano and dicyanovinyl-substituted oligomers as organic semiconductors

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ABSTRACT

Thiophene-phenylene co-oligomers with cyano and dicyanovinyl substituents at different positions were synthesized. Their stability and energy levels were estimated through thermal gravimetric analysis, UV–vis absorption spectra and electrochemistry. Interestingly, the absorption of BTCV covered the range of 430–610 nm, and thin film transistors of BTCV exhibited p-type behavior with high stability, suggesting BTCV a good candidate for solar cell.

1. Introduction

Conjugated oligomers are one of the most important classes of organic semiconductor materials and have found wide applications in organic field effect transistors (OFETs), solar cells, organic light emitting diodes (OLED) and so on [1]. As organic semiconductor materials, oligomers usually have good solubility and are facile to be modified, so that their property can be modulated easily to fit various applications. Electron-donating and electron-withdrawing groups are widely used to tune the energy level and property of oligomers. And the intermolecular interactions and thin film morphology of oligomers sometimes changed dramatically when an electron-donating or electron-withdrawing substituent was introduced [2]. Moreover, the position of these substituents on oligomers could make different effects on oligomer's electronic properties [3]. So it is very important for material science to study the effect of electron-donating or electron-withdrawing substituents to the property of oligomers.

Cyano and dicyanovinyl substitutents are common electron-withdrawing groups. Literatures reported organic semiconductors with cyano groups at different position showed different electroluminescent behaviors in OLED and photophysical properties in solar cells [4]. Recently, it was reported the introduction of cyano groups could alter the molecular stacking and crystalline properties of oligomers [5]. Dicyanovinyl substituent $-CH{=}C(CN)_2$ as strong electron-withdrawing group was often used in nonlinear optical materials and OLEDs [6]. It was found that the introduction of dicyanovinyl substituent could enhance absorption intensity and enlarge absorption range of oligomers, and thus improve the power conversion efficiency in solar cells [7]. Dicyanomethylene substituent, which has similar electron-withdrawing property to dicyanovinyl substituent, has been used as electron-withdrawing group to induce n-type behavior in OFET and mobility as high as $0.2\,cm^2\,V^{-1}\,s^{-1}$ was obtained [8]. Comparing with dicyanomethylene, dicyanovinyl substituent was comparatively easily synthesized. More important, unlike dicyanomethylene substituent, dicyanovinyl group did not alter the aromaticity of the linked rings, which would highly improve the environmental stability of the materials.

From the above facets, it suggested that cyano and dicyanovinyl groups play versatile roles in modulating the material's property. In order to further investigate the effect of these electron-withdrawing substituents to the property of oligomers, in this manuscript, phenylene-thiophenes co-oligomers containing different number of $-CN$ and $-CH{=}C(CN)_2$ substituents on different position (Scheme 1) were synthesized and their properties were investigated.

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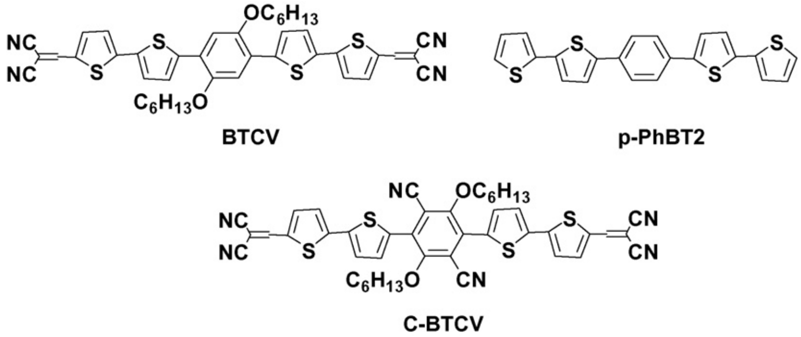


Scheme 1. Chemical structures of BTCV, C-BTCV and comparison compound p-PhBT2.

2. Experiments

2.1. General

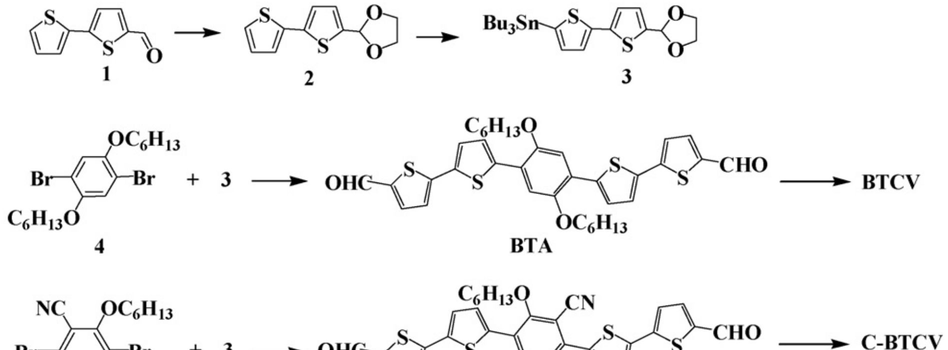
Chemicals and reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Benzene and toluene were distilled from sodium/benzophenone. Dichloromethane were distilled from P_2O_5. The melting points were measured on XT4-100X microscope apparatus without calibration. ^{1}H NMR spectra were obtained on a DMX-400 NMR spectrometer using tetramethylsilane (0.2%) as the internal reference. UV–vis absorption spectra were recorded on a Hitachi U3500 spectrometer. Electrochemistry was conducted in dichloromethane in a conventional three-electrode cell on CHI660C instruments at room temperature with Bu_4NPF_6 as supporting electrolyte, Ag/AgCl as the reference electrode, a platinum wire as the counter electrode, and glassy carbon disk as the working electrode. Ferrocene was adopted to calibrate the redox peak voltage. The scan rate was 100 mV/s. Thermal gravimetric analysis (TGA) measurements were carried out on a TA SDT 2960 instrument under nitrogen heating from room temperature to 550 °C with a heating rate of 10 °C/min. Organic filed effect transistors (OFETs) characteristics were recorded by a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a clean and shielded box.

2.2. Materials syntheses

Compound **2**. A three-neck flask equipped with a Dean-stark apparatus was charged with 5-formyl-2-2′-bithiophene **1** (2.91 g, 15 mmol), p-toluenesulfonic acid monohydrate (0.57 g, 3 mmol), ethylene glycol (18.6 g, 300 mmol) and 200 mL benzene. The reaction mixture was refluxed for about 24 h and the resulted azeotropic water was removed. After cooled to room temperature, saturated sodium hydrogen carbonate aqueous (150 mL) was added. The mixture was extracted with benzene, dried with $MgSO_4$. After evaporation of the solvent, **2** was obtained as light-yellow oil. Yield, 3.57 g (~100%)). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.21 (d, $^2J = 5.1$ Hz, 1H) 7.16 (d, $^2J = 3.6$ Hz, 1H), 7.06–7.04 (dd, 2H), 7.10 (dd, 1H), 6.09 (s, 1H), 4.14 (t, 2H), 4.03 (t, 2H). MS (EI): m/z 238 (M^+).

Compound **3**. A solution of **2** (2.38 g. 10 mmol) in THF was degassed with N_2 thoroughly and cooled to −78 °C for about 15 min. n-BuLi (4.2 mL, 2.5 M in hexane) was added slowly. The reaction mixture was stirred for about 1.5 h, then tributylstannyl chloride (3.9 g, 12 mmol) was added. The mixture was allowed to warm to room temperature and stirred for further 1.5 h. Most of the solvent was removed, and brine was added. The mixture was extracted with dichloromethane (80 mL × 3), dried with $MgSO_4$. After evaporation of solvents, the residue was purified through flash column chromatography (alumina, 1:1 petroleum ether-dichloromethane) to give compound **3** as light-yellow oil. Because of the instability, compound **3** was used directly without further purification. MS (EI): m/z 528 (M^+).

Compound BTA. A mixture of **3** (500 mg, 0.95 mmol), **4** (207 mg, 0.47 mmol), $Pd(PPh_3)_2Cl_2$ (26 mg, 0.04 mmol), PPh_3 (20 mg, 0.08 mmol) in 10 mL toluene was refluxed overnight under N_2 atmosphere. Then concentrated hydrochloric acid (10 mL) was added, the mixture was stirred at room temperature for 1 h and extracted with dichloromethane. The extract was washed with water and dried with $MgSO_4$. Solvent was removed and BTA was purified through recrystallization in dicholormethane. Yield, 0.22 g (70%). Mp 184–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 9.87 (s, 2H), 7.69 (d, $^2J = 4.0$ Hz, 2H), 7.52 (d, $^2J = 4.0$ Hz, 2H), 7.37 (d, $^2J = 4.0$ Hz, 2H), 7.30 (d, $^2J = 4.0$ Hz, 2H), 7.28 (s, 2H), 4.15 (t, $^3J = 6.5$ Hz, 4H), 1.99–1.92 (p, 4H), 1.62–1.57 (p, 4H), 1.42–1.36 (m, 8H), 0.93 (t, $^3J = 6.9$ Hz,



Scheme 2. Synthetic routes for BTCV and C-BTCV.