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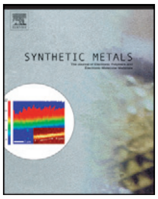

A polythiophene derivative with octyloxyl triphenylamine-vinylene conjugated side chain: Synthesis and its applications in field-effect transistor and polymer solar cell

Yingping Zou[a,b], Guangyi Sang[a,b], Weiping Wu[a,b], Yunqi Liu[a,*], Yongfang Li[a,*]

[a] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100039, China

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ABSTRACT

A new polythiophene derivative with octyloxyl triphenylamine-vinylene (**OTPAV**) conjugated side chain, **OTPAV-PT**, was synthesized according to the Stille coupling method, and characterized by ^{1}H NMR, elemental analysis, GPC, TGA, UV–vis absorption spectroscopy, photoluminescence spectroscopy, and cyclic voltammetry. The polymer possesses excellent solubility in common organic solvents and good thermal stability with 5% weight loss temperature of 413 °C. The weight-average molecular weight of **OTPAV-PT** was 1.04×10^4 with the polydispersity index of 1.45. Polymer solar cell with the configuration of ITO/PEDOT:PSS/**OTPAV-PT**:PCBM/Al was fabricated, and the power conversion efficiency of the device was 0.21% under the illumination of AM1.5, 100 mW/cm^2. The field effect hole mobility of the polymer reached 1.6×10^{-4} cm^2 V^{-1} s^{-1}.

1. Introduction

In recent three decades, there are broad interests in the synthesis of conjugated polymers because of their promising applications in light-emitting diodes [1–3], chemical sensors [4,5], field effect transistors [6,7] and photovoltaic devices [8–12]. Among the various applications of conjugated polymers, polymer solar cells (PSCs) are more attractive because of the importance of solar energy utilization and its advantages of low cost, light weight, easy preparation and the possibility to fabricate flexible devices. For the application of the conjugated polymers in PSCs as electron donor, broad absorption in the visible region and higher hole mobility of the conjugated polymers are crucial for efficient photovoltaic materials. It is well known that the increase of effective conjugation length will broaden the absorption of π-conjugated polymers, thus, our group recently synthesized a series of polythiophene and poly(thienylene vinylene) derivatives with conjugated phenylene-vinylene [13], thienylene-vinylene [8,14], terthiophene-vinylene [15] or phenothiazine vinylene side chains [16]. The polymers with the conjugated side chains showed broad absorption in the visible region and higher hole mobility [8,13–16].

Organic field effect transistors (OFETs) attracted much interest recently because of their promising applications in organic sensors, integrated circuit, low-cost large area memories, smart cards, and driving circuits for large-area displays [16,17]. One of the most important aspects for OFETs is that they can be fabricated by easy patterning techniques at low cost and have good compatibility with flexible plastic substrates. Thus the solution processable polymers are preferable for the applications in OFETs.

An important characteristic of conjugated polymers is the easy modification of their molecular structure and properties by side chain substitution or copolymerization. Triphenylamine (TPA) is a well-known hole transporting unit [18]. In order to further investigate the effect of side-chain structure on the property of the polythiophene derivatives with conjugated side chains, here we synthesized a new polythiophene derivative with TPA unit as the conjugated side chains, **OTPAV-PT** (see Scheme 1), via the Stille coupling reaction. Polymer solar cell with the configuration of ITO/PEDOT:PSS/**OTPAV-PT**:PCBM (1:1, w/w)/Al was fabricated, and the power conversion efficiency of the device was 0.21%. Organic field effect transistors (OFETs) were also fabricated using **OTPAV-PT** as a new p-type channel material and characterized. The hole field effect mobility of the polymer was 1.6×10^{-4} cm^2 V^{-1} s^{-1} with the bare SiO$_2$/Si substrate, which is

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* Corresponding author. Tel: +86 10 62536989, fax: +86 10 62559373.
E-mail addresses: liuyq@iccas.ac.cn (Y. Liu), liyf@iccas.ac.cn (Y. Li).

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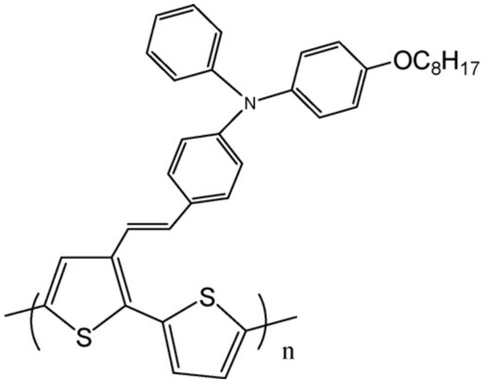

Scheme 1. Chemical structure of **OTPAV-PT**.

an order higher than that of the common polythiophenes (ca. 10^{-5} cm^2 V^{-1} s^{-1}).

2. Experimental

2.1. Materials

3-Methyl thiophene, phenanthroline, 4-iodophenol and diphenylamine were purchased from Aldrich Chemical Co., $Pd(Ph_3)_4$, $(C_4H_9)_3SnCl$, BuLi were obtained from Alfa Asia Chemical Co., and they were used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Toluene was dried over molecular sieves and freshly distilled prior to use. The other chemical reagents were common commercial products and used as received without further purification.

2.2. Characterization

^{1}H NMR spectra were recorded using a Bruker AV400 spectrometer. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a BIO FTS-135 spectrometer by dispersing samples in KBr disk. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)) using THF as eluent at a flow rate of 1.0 mL/min at 35 °C. Thermogravimetric analysis (TGA) was conducted on a DTG-60 thermogravimetric analyzer with a heating rate of 10 K/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was recorded with a Thermal Analysis (TA) DSC-2010 in nitrogen. UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. The photoluminescence (PL) spectra were obtained with a JASCO FP-6600 Fluorescence spectrophotometer. Cyclic voltammogram was recorded with a computer controlled Zahner IM6e electrochemical workstation (Germany) with polymer film on platinum disk as the working electrode, platinum wire as the counter electrode and Ag/Ag^+ (0.1 M) as the reference electrode.

2.3. Fabrication and characterization of polymer solar cell

The polymer solar cells were fabricated in the configuration of the traditional sandwich structure with ITO positive electrode and metal negative electrode. The ITO glass was cleaned in an ultrasonic bath of acetone and isopropanol, and then treated in boiled H_2O_2. A thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron, PVP 4083, Germany) was spin-coated on the ITO glass and dried in vacuum oven at 120 °C for 20 min. The thickness of the PEDOT:PSS layer was ca. 30 nm. Subsequently, the active layer was prepared by spin coating the *o*-dichlorobenzene solution of polymer **OTPAV-PT**:PCBM (1:1, w/w) with the polymer concentration of 10 mg mL^{-1} on the top of the PEDOT:PSS layer, giving a thickness of ca. 70 nm determined by a surface profilometer (XP-2, USA). The Al electrode (100 nm) was thermally deposited on the active layer through a mask at a pressure of 5×10^{-5} Pa. The active area of a device was 4 mm^2.

The current–voltage (*I*–*V*) measurement of the PSCs was conducted on a computer-controlled Keithley 236 source measure unit. A Xenon lamp with AM1.5 filter was used as a white-light source and the optical power was 100 mW/cm^2. All the measurements were automatically controlled by a computer system, and performed under ambient atmosphere at room temperature.

2.4. Fabrication of OFET devices

Thin-film OFETs were fabricated with top-contact configuration. An n-doped Si wafer with a thermally grown silicon dioxide layer (thickness of 450 nm, capacitance of 10 nF/cm^2) was used as the substrate. The substrates were cleaned in water, alcohol, acetone, and rinsed in deionized water. Thin polymer films were prepared by spin coating of a 0.3 wt% solution of **OTPAV-PT** in chloroform onto the bare SiO_2/Si substrates at a speed of 3000 rpm (revolutions per minute) for 40 s at room temperature. After dried at 80 °C and annealed at 150 °C under N_2 for half an hour, gold film (50 nm) was deposited on the organic layer to form the drain and source electrodes, for a typical device, the drain-source channel length (*L*) and width (*W*) are 50 μm and 3000 μm, respectively. OFET measurements were performed at room temperature using a HP 4140B semiconductor parameter analyzer under ambient conditions.

2.5. Synthesis of monomers and polymer

The synthetic route of the monomers and polymer are shown in Scheme 2. The detailed synthetic procedures are as follows.

2.5.1. 1-Octyloxyl-4-iodobenzene (**1**)

To a stirred mixture of 4-iodophenol (22 g, 0.1 mol), octylbromide (19 g, 0.1 mol) and DMF (100 mL) was added K_2CO_3 (20.7 g, 0.15 mol) under argon. The reaction proceeded for 15 h at 150 °C, then cooled to room temperature. The resulted mixture was filtered, and then extracted with chloroform. The organic layer was washed with a dilute solution of KOH and water, dried over anhydrous magnesium sulfate, filtered, and purified with column chromatography (silica gel, petroleum ether as eluent) to yield 29 g (87%) of 1-octyloxyl-4-iodobenzene as colorless oil. MS: $m/z = 332(M^+)$. ^{1}H NMR (δ/ppm, $CDCl_3$): 0.88–0.93 (m, 3H), 1.28–1.48 (m, 10H), 1.68–1.70 (m, 2H), 3.80–3.82 (d, 2H), 6.67–6.68 (d, 2H), 7.51–7.53 (d, 2H).

2.5.2. 4-Octyloxy-triphenylamine (**2**)

The mixture of **1** (9.9 g, 30 mmol), diphenylamine (6.0 g, 36 mmol), CuCl (0.2 g, 2 mmol), phenanthroline (0.26 g, 1.44 mmol), KOH (13.4 g, 0.24 mol) and toluene (60 mL) was reacted at 130 °C for 36 h. After cooling, the resulted mixture was poured into plenty of stirred water, and extracted with chloroform. The obtained organic phase was washed several times with water, dried over magnesium sulfate, evaporated, and purified with column chromatography (silica gel, petroleum ether as eluent) to yield 10.5 g (93.7%) of 4-octyloxy-triphenylamine as a colorless oil. MS: $m/z = 373(M^+)$. ^{1}H NMR (δ/ppm, $CDCl_3$): 7.30–6.77 (14H, m), 3.93 (2H, t), 1.78–1.25 (12H, m), 0.90 (3H, t).