

Synthesis and Photovoltaic Properties of Polythiophene Derivatives with Side Chains Containing C₆₀ End Group

Youjun He,^{1,2} Jianhui Hou,¹ Zhan'ao Tan,¹ Yongfang Li¹

¹Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

²Graduate University of Chinese Academy of Sciences, Beijing 100039, China

Received 13 August 2008; accepted 1 June 2009

DOI 10.1002/app.30863

Published online 8 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A donor–acceptor double-cable polythiophene derivative (**PT-F1**) with side chain containing C₆₀ end group was synthesized, and characterized by infrared, UV-vis absorption and photoluminescence (PL) spectroscopy, and electrochemical cyclic voltammetry. Cyclic voltammogram of **PT-F1** shows the oxidation peak of the polymer main chains and the reduction peaks of the C₆₀ end groups, indicating that there is no interaction between the polymer main chains and side chain C₆₀ groups on the ground state. The UV-vis absorption spectrum of **PT-F1** film is red-shifted in comparison with that

of its chloroform solution. The PL spectrum of the polymer main chain was quenched by the C₆₀ pendant on the side chain. Polymer solar cell with the structure of ITO/PEDOT:PSS/**PT-F1**/Ca/Al was fabricated. The power conversion efficiency of the device based on **PT-F1** reached 0.274% under the illumination of AM 1.5, 100 mW/cm². © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 532–539, 2010

Key words: donor–acceptor double-cable polymers; polythiophene derivatives; polymer solar cells

INTRODUCTION

Conjugated polymer photovoltaic materials and polymer solar cells (PSCs) have drawn great attention in recent years,^{1–3} because of the importance of energy source and the advantages of low cost, easy fabrication, light weight, and flexibility of the PSCs. The PSCs are usually composed of a bend film of conjugated polymer donor (D) and the soluble C₆₀ derivative PCBM acceptor (A) as the active layer sandwiched between a transparent ITO positive electrode and a low work function metal negative electrode. The morphology of the D/A interpenetrating network in the active layer is of crucial importance for the efficient operation of these systems,^{4–6} and one of the problems influencing the power conversion efficiency of the PSCs is the phase separation of the fullerene and polymer into discrete domains. This phase-separation problem could be overcome by covalently linking the fullerene moiety to the polymer backbone in a so-called double-cable molecular structure.⁷

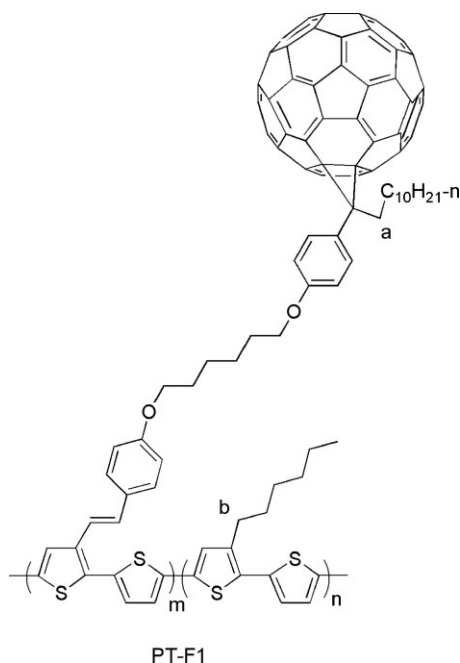
Solution-processable^{8–11} and electropolymerized^{8,12–14} conjugated polymers with pendant fullerenes have been proposed. Also, dyads with the full-

erene linked to conjugated oligomers have been synthesized and tested in photovoltaic devices.^{15–29} Most of the work was concentrated on the interaction between polythiophene part and fullerene in double-cable polymers,^{29,30} and the results display that polythiophene part and fullerene pendant part keep their ground state properties independently. Antonio Cravino fabricated a photovoltaic device using their double-cable polythiophene³¹ as the active layer, they found the open-circuit voltage declined and short-circuit current increased over several orders of magnitude after polythiophene was pendant with fullerene, and the solubility of double-cable polymers becomes worse with the increasing of fullerene content in the double-cable polymers.³¹ Some oligo-thiophenes with fullerene are used as the active layer in the photovoltaic devices, but the power conversion efficiency is very low in these kinds of devices because of double-cable polymer's poor solubility, even the highest one is only 0.64%²³ under the illumination of 10 μW/cm² monochromatic light at 466 nm. With regard to the bulk heterojunction solar cell using polythiophene and fullerene derivatives as the active layer (over 5%),^{32,33} its power conversion efficiency is still very low, the main reason to this phenomenon is the poor solubility and lower electron transportation efficiency of the double-cable polymers.⁸

Recently, our group synthesized a double-cable polythiophene (**PT-F**)³⁴ and fabricated the photovoltaic device based on **PT-F**, the power conversion

Correspondence to: Y. Li (liyf@iccas.ac.cn).

Contract grant sponsor: NSFC; contract grant numbers: 20721061, 50633050.



Scheme 1 Molecular structure of the soluble double-cable polythiophene **PT-F1** ($m : n = 0.50 : 0.50$).

efficiency of the device reached 0.52% under AM 1.5, 100 mW/cm². In this article, we synthesized a new polythiophene derivative with the same fullerene side chain as **PT-F** but different main chain (as shown in Scheme 1, **PT-F1**). The motivation of this work is to improve the absorption and solubility of the double-cable polymers. The photovoltaic devices based on the single-component **PT-F1** were fabricated and characterized.

EXPERIMENTAL

Materials

3-Hexylthiophene (**5**) and 2,5-dibromo-3-hexylthiophene (**6**) were prepared according to literature procedure.³⁵ 2,5-Bis(tributylstannyl) thiophene was prepared according to literature procedure.³⁶ All other reagents were common commercial level and used as received.

Measurement and characterization

¹H-NMR spectra were measured on a Bruker DMX-300 spectrometer; all chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer by dispersing samples in KBr disks. Elemental analysis was carried out on a Flash EA 1112 elemental analyzer. Molecular weights and polydispersity of the polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration [Waters 515 HPLC pump,

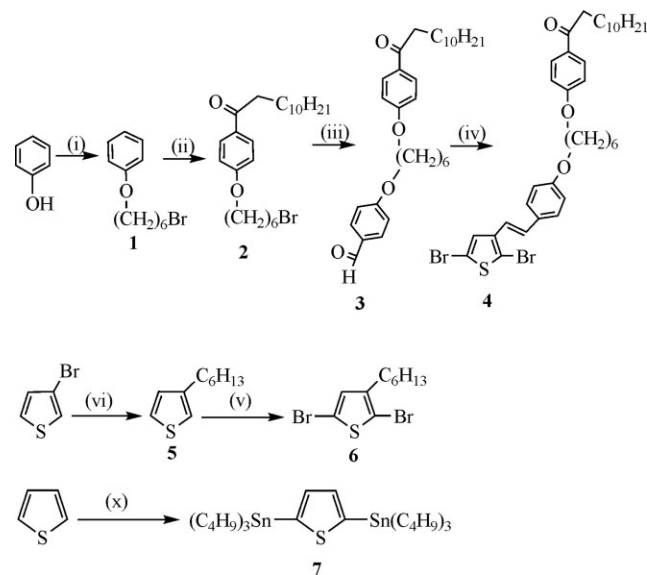
a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)] using THF as eluent at a flow rate of 1.0 mL/min at 35°C. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with Pt disk, Pt plate, and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution.

Synthesis of monomers and Polymers

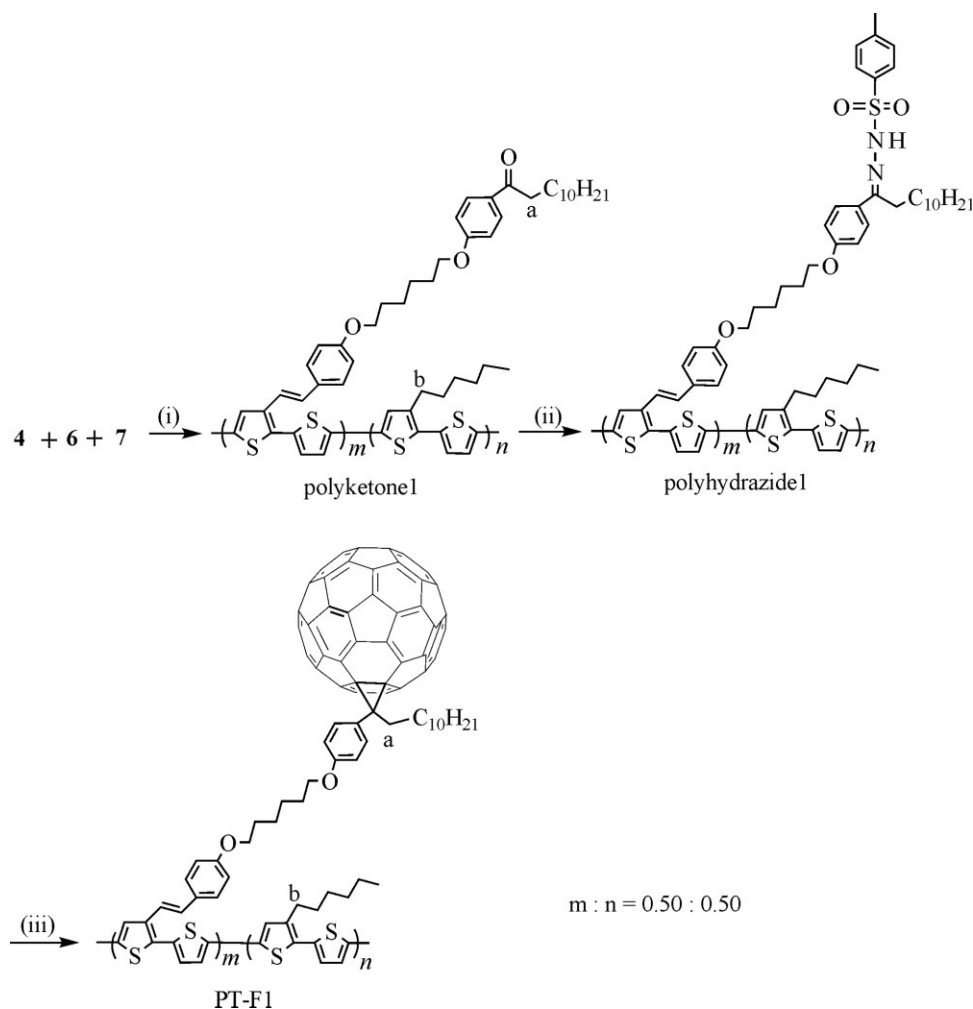
The synthetic routes of monomers and polymers are shown in Scheme 2 and Scheme 3, respectively.

1-(6-Bromohexyloxy) benzene, **1**

KOH (5.60 g, 0.10 mol) was added to a water (50 mL) solution of phenol (9.40 g, 0.10 mol). 1,6-dibromohexane (96.80 g, 0.40 mol) was added to the reaction mixture in one portion. The reactant was heated to reflux and stirred for 12 h. Then, the organic layer was separated and washed for three times with water. Distillation under vacuum gave colorless 1-(6-bromohexyloxy) benzene (20.60 g,



Scheme 2 Synthetic routes of monomers. (i) Br(CH₂)₆Br, KOH, H₂O, reflux for 12 hs; (ii) Dodecanoyl chloride, AlCl₃, CH₂Cl₂, ambient temperature, overnight; (iii) 4-hydroxybenzaldehyde, K₂CO₃, DMF, 80°C, 6 hs; (iv) 2,5-dibromo-3-bromomethylthiophene, P(OC₂H₅)₃, 160°C for 2 hs, then compound **3**, CH₃ONa, DMF, cool water bath, 30 min; (v) NBS, CHCl₃, HOAc; (vi) C₆H₁₃ MgBr, Ni(dppp)Cl₂, THF, reflux; (x) thiophene, *n*-butyl lithium, THF reflux for 2 hs, then Sn(C₄H₉)₃Cl, ambient temperature for 12 hs.



Scheme 3 Synthetic route of PT-F1. (i) Compound 4,7, Pd(PPh₃)₄, toluene, argon, reflux for 12 hs; (ii) polyketone1, *p*-tosylhydrazine, trace amount of HCl, THF, reflux for 6 hs; (iii) polyhydrazide1, CH₃ONa, pyridine, stirred for 15 min, then C₆₀ in *o*-dichlorobenzene, reflux for 24 hs under nitrogen.

0.08 mol). Yield: 80.47%. GC-MS: $m/z = 256$ (M⁺). ¹H-NMR (CDCl₃) $\Delta = 7.21$ (t, 2H), 6.92 (d, 1H), 6.75 (d, 2H), 3.85 (t, 2H), 3.15 (t, 2H), 1.81 (m, 2H), 1.72 (m, 2H), 1.33 (m, 4H). C₁₂H₁₇OBr: Calcd. C 56.25, H 6.64; Found: C 56.17, H 6.56.

1-Dodecanoyl-4-(6-bromohexyloxy) benzene, 2

Under ice-bath, **1** (27.00 g, 0.11 mol) was added to a 250 mL three-necked flask equipped for stirring. Anhydrous aluminum trichloride powder (14.00 g, 0.11 mol) was added to the above flask. Dodecanoyl chloride (23.98 g, 0.11 mol) was drop-added to the system under 0°C. Then reacted for one night under room temperature, pledged the reaction mixture into ice, extracted with chloroform, and removed the solvent. Then the re-crystallization with methanol gave white solid **2** (27.00 g, 0.060 mol). Yield: 56.04%. GC-MS: $m/z = 438$ (M⁺). ¹H-NMR (CDCl₃) $\Delta = 7.92$ (d, 2H), 6.96 (d, 2H), 3.96(t, 2H), 3.40(t, 2H), 2.90(t, 2H), 1.91 (m, 2H), 1.84 (m, 2H), 1.73 (m, 2H), 1.51 (m,

6H), 1.30–1.25 (m, 14H), 0.91 (m, 3H). C₂₄H₃₉BrO₂: Calcd. C 65.75, H 8.90. Found: C 65.50, H 8.76.

4-(6-(4-Dodecanoyl phenoxy)hexyloxy) benzaldehyde, 3

Benzaldehyde (12.20 g, 0.10 mol) was dissolved in 40 mL DMF in a 100 mL one-necked flask equipped for stirring. Potassium hydroxide (5.60 g, 0.10 mol) was added to the solution, and the solution was stirred for several minutes. Then **2** (27.00 g, 0.060 mol) was added, the mixture was stirred for about 5 h at 120°C. The solution was pledged into water, and then filtrated, washed with methanol. The filter mass was recrystallized with methanol, got white solid **3** (16.03 g, 0.030 mol). Yield: 33.40%. GC-MS: $m/z = 480$ (M⁺). ¹H-NMR (CDCl₃) $\Delta = 9.87$ (s, 1H), 7.93 (d, 2H), 7.81 (d, 2H), 6.98 (d, 2H), 6.90 (d, 2H), 4.05 (t, 2H), 4.03 (t, 2H), 2.89 (t, 2H), 1.85 (m, 4H), 1.74 (m, 2H), 1.56 (m, 4H), 1.31–1.23 (m,

16H), 0.91 (t, 3H). $C_{31}H_{44}O_4$: Calcd. C 77.55, H 9.17; Found: C 77.30, H 9.42.

3-(4-(6-(4-Dodecanoyl phenoxy)hexyloxy)styryl)-2,5-dibromothiophene, 4

2,5-Dibromo-3-bromomethylthiophene (3.35 g, 0.01 mol) and phosphorus acid triethyl ester (1.66 g, 0.01 mol) were put in a flask and heated to 160°C for 2 h. The product of 2,5-dibromothiophen-3-ylmethyl phosphonic acid diethyl ester was obtained and used directly without any purification. Then the product and compound 3 (4.80 g, 0.01 mol) were dissolved in 30 mL of dried DMF. Under a cool water bath, $NaOCH_3$ (0.6 g in 10 mL of DMF) was added dropwise into the solution. After 30 min, the solution was poured into 100 mL of methanol and filtered after being cooled to -5°C. The product of compound 4 was purified by re-crystallization from methanol and obtained as a white solid (5.04 g, 0.0070 mol). Yield: 70.39%. C-Ms: $m/z = 716$ (M^+). 1H -NMR ($CDCl_3$) $\Delta = 7.92$ (d, 2H), 7.41 (d, 2H), 7.19 (s, 1H), 6.92–6.85 (m, 6H), 4.03 (t, 2H), 4.01 (t, 2H), 2.91 (t, 2H), 1.85 (m, 4H), 1.74 (m, 2H), 1.56 (m, 4H), 1.35–1.29 (m, 16H), 0.91 (t, 3H). $C_{36}H_{46}Br_2O_3S$: Calcd. C 60.34, H 6.42, Br 22.07, O 6.70, S 4.47; Found: C 60.43, H 6.47, Br 22.01, O 6.82, S 4.27.

3-Hexylthiophene, 5

Under N_2 atmosphere, magnesium turnings (2.60 g, 0.11 mol) was put into a 250 mL flask and 40 mL dried ether was charged. 1-bromo-hexane (16.50 g, 0.10 mol) was dissolved into 40 mL ether and added into the flask through a dropping funnel. When the reaction subsided, a gray solution of hexyl-magnesium bromide was obtained. In another flask, 3-bromo-thiophene (16.30 g, 0.10 mol) and 30 mL ether were charged, and $NidpppCl_2$ (0.25 g, 0.50 mmol) was added. Under an ice-water cooling bath, the hexyl-magnesium bromide was added dropwise, and when the addition was ended, the reactant was heated to reflux. After 12 h, the reaction was quenched by the addition of 100 mL HCl (2 mol/L). The organic layer was separated, and the aqua layer was extracted by ether. All of the organic layers were combined, washed with water, and dried over anhydrous $MgSO_4$. After the removal of solvent, 3-hexylthiophene (12.08 g, 0.072 mol) was obtained under decompression. Yield: 71.90%. 1H -NMR ($CDCl_3$) $\Delta = 7.06$ (d, 1H), 6.75 (s, 1H), 6.74 (d, 1H), 2.55 (t, 2H), 1.62 (m, 2H), 1.30(m, 6H), 0.95 (t, 3H).

2,5-Dibromo-3-hexylthiophene, 6

Compound 5 (8.40 g, 0.050 mol) was dissolved into 40 mL $CHCl_3$ and NBS (17.80 g, 0.10 mol) was

added. The reactant was heated to reflux for 2 h, and the mixture was poured into 200 mL water and subtracted by 50 mL chloroform. The organic layer was washed with water and dried over $MgSO_4$. After the removal of solvent, 2,5-dibromo-3-hexylthiophene (13.80 g, 0.042 mol) was purified by distillation under decompression. Yield: 84.66%. 1H -NMR ($CDCl_3$) $\Delta = 7.01$ (s, 1H), 2.60 (t, 2H), 1.62 (m, 2H), 1.30 (m, 6H), 0.95 (t, 3H).

2,5-Bis(tributylstannyl) thiophene, 7

Thiophene (8.40 g, 0.10 mol) was dissolved in 60 mL of THF in a well-dried flask under the protection of nitrogen. *n*-Butyl lithium (76 mL, 0.22 mol, 2.88M in hexane) was added dropwise (caution: a great deal of gas evolved), and the solution was stirred at reflux for 2 h. After being cooled to ambient temperature, tributylchlorostannane (68.04 g, 0.21 mol) was added in one portion. After 12 h, the solution was poured into 100 mL of cool water. The organic layer was separated, and the aqua layer was extracted by ether. The organic layers were collected and dried over anhydrous $MgSO_4$, and the removal of solvent gave a crude product. 2,5-Bis(tributylstannyl) thiophene (35.03 g, 0.053 mol) was obtained after distillation under vacuum (0.1 mmHg/190°C). Yield: 53.08%. Purity (by GC) >96%. GC-Ms: $m/z = 664$ (M^+). 1H -NMR ($CDCl_3$) $\Delta = 7.34$ (s, 2H), 1.60 (m, 12H), 1.39 (m, 12H), 1.09 (m, 12H), 0.91 (t, 18H).

Polyketone1

Dry toluene (10 mL) was added to a 50 mL dry two-necked flask, then 4 (0.72 g, 1 mmol), 6 (0.33 g, 1 mmol), and 7 (1.32 g, 2 mmol) were added, provided with N_2 inlet during 20 min. Subsequently, $Pd(PPh_3)_4$ (20 mg) was added, provided with N_2 inlet during 10 min. The reaction mixture was stirred at 110°C during 16 h. Methanol (40 mL) was added dropwise to make polymer deposit in the mixture solvent of toluene and methanol. The mixture was transferred to a 50 mL centrifuge tube, and then was immersed in an ultrasonic bath for 1 min. The suspension was centrifuged, the supernatant was decanted, and the residue was treated with methanol (80 mL) twice in the same manner. The pellet was washed with methanol by using a Soxhlet extractor during 24 h, and then washed with hexane during 24 h. The polymer was then dissolved by Soxhlet extraction with THF, the THF was removed, and the residue was dried under vacuum to yield polyketone1 (520 mg).

Polyketone1, 1H -NMR ($CDCl_3$) $\Delta = 7.90$ (d, 2H), 7.43(d, 2H), 7.31(d, 2H), 7.19(s, 2H), 7.09(d, 2H), 6.90–6.86(m, 6H), 4.00(t, 4H), 2.88(t, 2H), 2.62(t, 2H), 1.82(m, 4H), 1.67(m, 4H), 1.54(m, 4H), 1.24(m, 22H),

0.87(t, 6H). From the integrate area of 2.88 ppm and 2.62 ppm, we can get the value of $m : n$ is 0.50 : 0.5. $C_{54}H_{64}O_3S_4$: Calcd. C 72.97, H 7.21, O 5.41, S 14.41; Found: C 72.76, H 7.09, O 5.62, S 14.12.

Polyhydrazide1

THF (70 mL) was added into a 100 mL one-necked flask, polyketone1 (500 mg) was dissolved, 4-methylbenzenesulfonylhydrazide (2.00 g, 0.011 mol) was added, and then four drops of HCl (2 m/L) were added, refluxed for 6 h. After removal of solvent, the residue was transferred to a 50 mL centrifuge tube. Then chloroform (4 mL) was added, and methanol (40 mL) was added drop wise. The mixture was immersed in an ultrasonic bath for 1 min, the suspension was centrifuged, and the supernatant was decanted. And the residue was treated with methanol (80 mL) twice in the same manner. The pellet was washed with methanol by using a Soxhlet extractor during 24 h, and then washed with hexane during 24 h. The polymer was dissolved by Soxhlet extraction with THF, after removal of THF, the residue was dried under vacuum to yield polyhydrazide1 (540 mg).

Polyhydrazide1, 1H -NMR ($CDCl_3$) $\Delta = 7.89$ (d, 2H), 7.76(d, 2H), 7.52(d, 2H), 7.43(d, 2H), 7.35(d, 2H), 7.18(s, 2H), 7.11(d, 2H), 6.89–6.85(m, 6H), 3.98(t, 4H), 2.75(t, 2H), 2.56(s, 1H), 2.41(s, 3H), 1.82(m, 4H), 1.68(m, 4H), 1.54(m, 4H), 1.40–1.24(m, 20H), 0.87(t, 6H). $C_{61}H_{72}O_4S_5N_2$: Calcd. C 69.32, H 6.82, O 6.06, S 15.15, N 2.65; Found: C 69.18, H 6.65, O 6.24, S 15.32, N 2.61.

The structure of polyhydrazide1 was proved by FT-IR spectra in Figure 1.

PT-F1

Polyhydrazide1 (510 mg) was dissolved in 30 mL of dry pyridine in a dried three-necked flask provided with N_2 inlet, a thermometer, and a magnetic stirring bar. Then, NaOMe (80 mg, 1.60 mmol) was added, and the mixture was stirred during 15 min. A solution of C_{60} (510 mg, 7.08 mmol) in 100 mL of dry 1,2-dichlorobenzene was added, and the homogeneous reaction mixture was stirred at 65–70°C during 22 h. The reaction mixture was transferred to a round bottom flask, the solvent was removed. The residue was washed with methanol by using a Soxhlet extractor during 24 h, and then washed with hexane during 24 h. The polymer was then dissolved by Soxhlet extraction with THF, the THF was removed, and the low molecular weight residue was achieved. Then, the polymer was dissolved by Soxhlet extraction with chlorobenzene, the chlorobenzene was removed, and then the high molecular weight fraction was dried under vacuum to yield PT-F1 (510 mg).

PT-F1: $C_{114}H_{64}O_2S_4$: Calcd. C 85.29, H 4.02, O 2.01, S 8.04; Found: C 85.73, H 4.13, O 2.08, S 8.01.

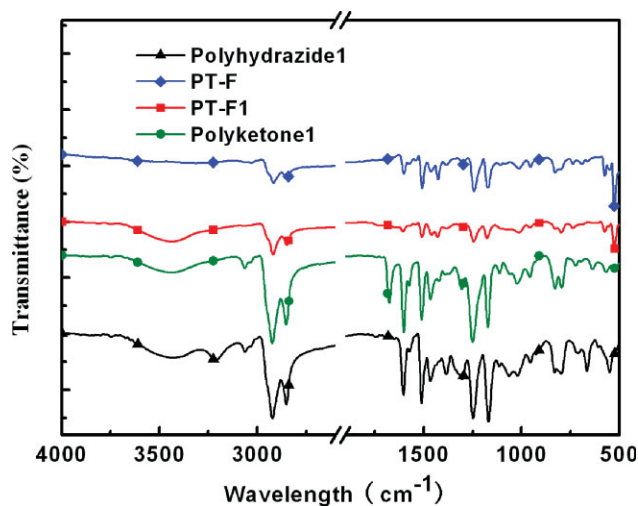


Figure 1 FT-IR spectra of polyhydrazide1, polyketone1, PT-F, and PT-F1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The elemental analysis result displays that nearly each repeated units of PT-F1 was substituted by one C_{60} molecule.

Device fabrication and characterization

The PSCs were constructed in the traditional sandwich structure through the following steps. Poly(3,4-ethylene dioxythiophene)-poly(styrene sulphonate) (PEDOT:PSS, from Bayer AG) was spin coated from an aqueous solution on a pre-cleaned indium tin oxide (ITO)/glass substrate giving a thickness of about 30 nm, and was dried subsequently at 150°C for 10 min. The photosensitive blend layer of polymer was prepared by spin-coating the chlorobenzene solution of the polymer with the concentration of 12 mg/mL on the ITO/PEDOT: PSS electrode, and dried at 80°C for 30 min, in a nitrogen-filled glove box. The cathode of devices, consisting of 10 nm of calcium and 150 nm of Aluminum, was thermally deposited on the top of polymer film at 5×10^{-5} Pa. The active area of the device is 4 mm². The current–voltage (I – V) measurement of the PSC devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A solar simulator was used as the light source; the light intensity was monitored by a standard Si solar cell.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic route of the double-cable polymer PT-F1 was shown in Scheme 3. For comparison, the polymers of polyketone1 and polyhydrazide1 (shown in Scheme 3), which possess a similar molecular structure with PT-F1 but without C_{60} end group on their side chains, were also analyzed and characterized.

The molecular structures of the polymers were characterized by FT-IR analysis. In the FT-IR spectra, as shown in Figure 1, polyketone1 exhibited a clear peak at 1675 cm^{-1} for ν_{CO} while polyhydrazide1 had no signal at that position and instead appeared a new peak of ν_{NH} at 3213 cm^{-1} . The FT-IR spectra give clear evidence of the molecular structures of polyketone1 and polyhydrazide1. The molecular structure of the double-cable polymer **PT-F1** was also confirmed by FT-IR (refer Fig. 1), and elemental analysis. In the FT-IR spectra, **PT-F1** shows four characteristic peaks of C_{60} at 523, 574, 1182, and 1426 cm^{-1} . The value of $m : n$ of polymers were estimated roughly by $^1\text{H-NMR}$ of polyketone1, the hydrogen on position **a** shows a peak at $\delta = 2.88$ ppm, and the hydrogen on position **b** shows a peak at $\delta = 2.62$ ppm. Hence, the values of $m : n$ could be calculated to be about 0.5 : 0.5 from the ratio of the integral areas of the two peaks. The roughness of the value of $m : n$ obtained depends on the overlap of the two peaks.

The weight-average molecular weights (M_w) of polyketone1 and polyhydrazide1 were 1.7×10^4 and 2.3×10^4 with the polydispersity index (PDI) of 1.7 and 2.0, respectively. The molecular weight of **PT-F1** is hard to be determined by GPC, since it cannot be solved in THF which is commonly used as eluent in GPC. According to the molecular weights of polyketone1 and polyhydrazide1, the M_w of **PT-F1** should be in the range of 20 K–40 K because C_{60} is connected with the polymer side chain without interruption of the polymer main chain during the synthesis of **PT-F1**.

Electrochemical properties

Figure 2 shows the cyclic voltammograms of the polymer films on Pt electrode in a 0.1 mol/L Bu_4NPF_6 , CH_3CN solution. In comparison with the cyclic voltammogram of polyketone1 (refer Fig. 2), the corresponding **PT-F1** after being substituted of polyketone1 with C_{60} exhibited the characteristic reduction peaks of C_{60} at -0.55 , -1.10 , -1.58 V versus Ag/Ag^+ (refer Fig. 2). This indicates that the electronic properties of C_{60} remained³⁷ and there is no interaction between the polythiophene main chains and the C_{60} on the side chains at the ground state.³⁴ The cyclic voltammogram of polyketone1 shows the onset oxidation potential at about 0.3 V versus Ag/Ag^+ and a onset reduction potential of about -1.91 V versus Ag/Ag^+ , which should be corresponding to the *p*-doping and *n*-doping of the polymer main chains, respectively. Obviously, the oxidation wave at higher than 0.3 V versus Ag/Ag^+ and the reduction wave at lower than -1.9 V versus Ag/Ag^+ in the cyclic voltammogram of **PT-F1** could be ascribed to the *p*-doping and *n*-doping of the **PT-**

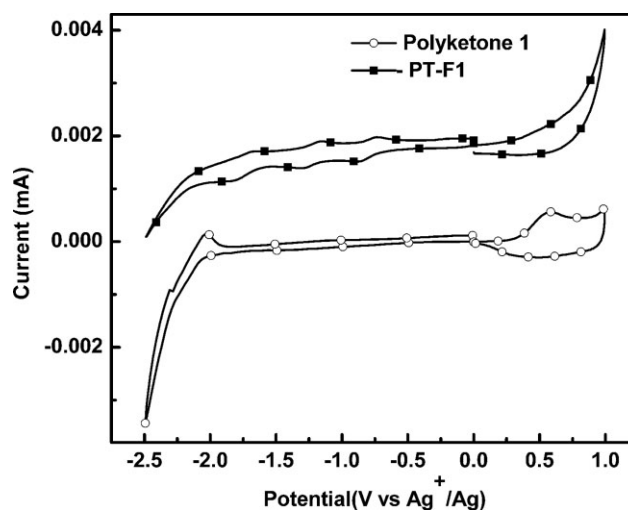


Figure 2 Cyclic voltammograms of polyketone1 and **PT-F1** films in Pt electrode infilms on Pt electrode 0.1 mol/L Bu_4NPF_6 , CH_3CN solution with a scan rate of 100 mV/s.

F1 main chains, respectively. The poor reversibility of the oxidation and reduction of **PT-F1** main chains could be due to the influence of its big side chains on the main chains.

Absorption and PL spectra

Figure 3 shows the absorption spectra of the polymers. It can be seen that the maximum absorption wavelength of polyketone1 and **PT-F1** in the visible region is 491 and 478 nm, respectively. The absorbance of **PT-F1** in the visible region decreased a lot than that of polyketone1. This is due to the strong absorbance in UV region of fullerene on the side chain and the steric effect of the big side chain on the polythiophene main chains of **PT-F1**, so that after linking fullerene to polythiophene main chain, the ratio of the visible absorption of the polymer main chains to the UV absorption of the side chains decreased. In addition, the absorption spectrum of double-cable polymer **PT-F1** solution could also be roughly thought as addition spectra of polyketone1 and C_{60} [refer Fig. 3(a)], which further indicates that polythiophene part and fullerene pendant part keep their ground state properties independently.

The maximum visible absorbance wavelength of polyketone1 and **PT-F1** films on quartz plate is 531 and 502 nm, respectively, as shown in Figure 3(b). The film absorption peaks red-shifted by 40 and 24 nm relative to those of their chloroform solutions, respectively, which is due probably to that the big volume of the side chains in the polymers, distort the polymer main chains in the solution state, and there is more planar conformation of the polymer main chains from π -stacking/aggregation in solid

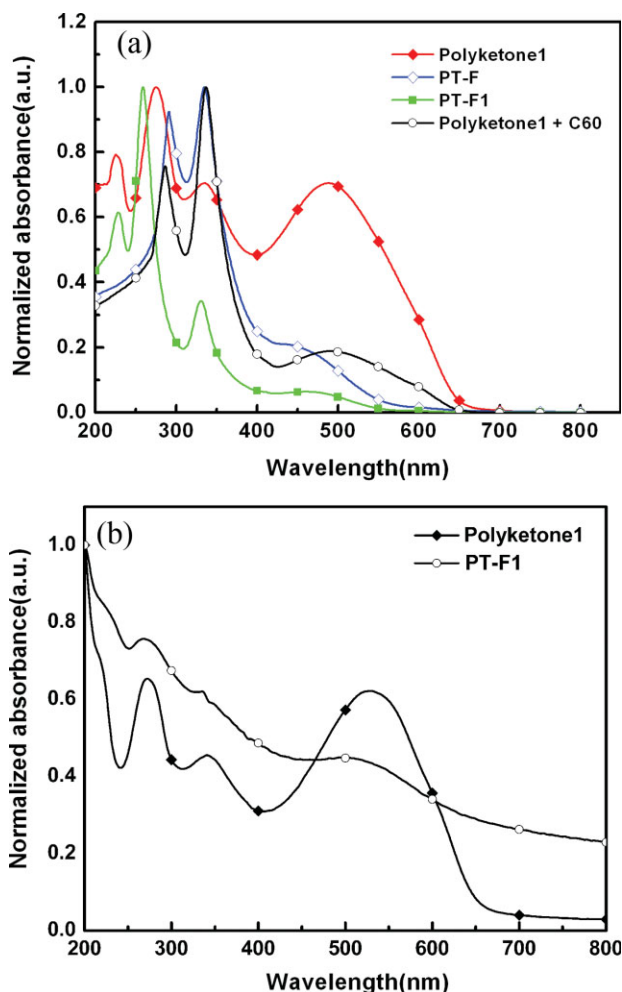


Figure 3 Absorption spectra of (a) the polymers solutions in chloroform and (b) the polymer films on quartz plate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

films. It is noteworthy that the absorption of PT-F1 film in the visible region is stronger than that of PT-F film,³⁴ indicating that the copolymerization with the bithiophene units in PT-F1 improved the visible absorption of the double-cable polymers.

Figure 4 shows the photoluminescence (PL) spectra of the polymer solutions in chloroform. There is strong photoluminescence of polyketone1 peaked at about 590 nm excited at 440 nm, but the photoluminescence of PT-F1 was quenched greatly. In comparison, there is no PL quenching in the dilute solution of polyketone1 and C₆₀, indicating that the charge transfer from the exciton of polyketone1 to C₆₀ is limited in the dilute solution. The PL quenching of PT-F1 should result from the photo induced electron transfer from PT main chains to C₆₀ moiety on the side chains. The results indicate that the double-cable polymers could be used as the photovoltaic material in a single-component photovoltaic cells.

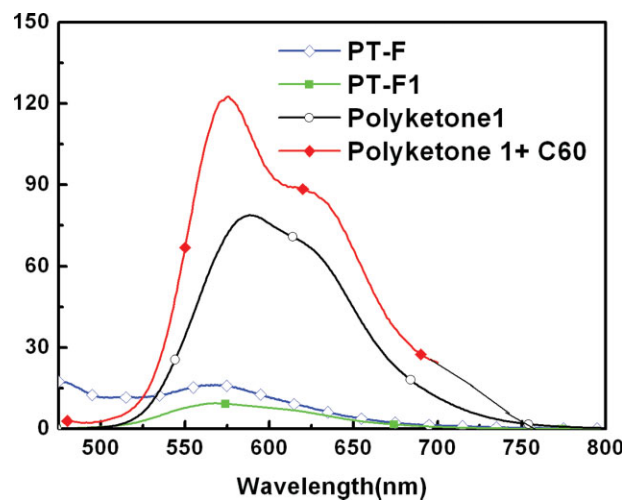


Figure 4 Photoluminescence spectra of the polymers in chloroform solutions (10^{-5} mol/L) excited at 440 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Photovoltaic property

Single-component polymer solar cells (PSCs) were fabricated with the structure of ITO/PEDOT: PSS (30 nm)/photosensitive layer (65 nm)/Ca (10 nm)/Al (150 nm), where the photoactive layer was prepared by spin-coating PT-F1 solution. Figure 5 shows the I - V curve of the device based on PT-F1. The photovoltaic properties of the device are as follows: the short-circuit current (I_{sc}) is 1.55 mA/cm^2 , the open-voltage (V_{oc}) is 0.63 V, fill factor (FF) is 0.281, and the power conversion efficiency (PCE) of the device is 0.274% under the illumination of AM 1.5, 100 mW/cm^2 . The PCE of 0.274% is among the high values for the single-component PSCs, but it is a little lower than that of the device based on PT-F.³⁴ Probably, the electron transfer between C₆₀

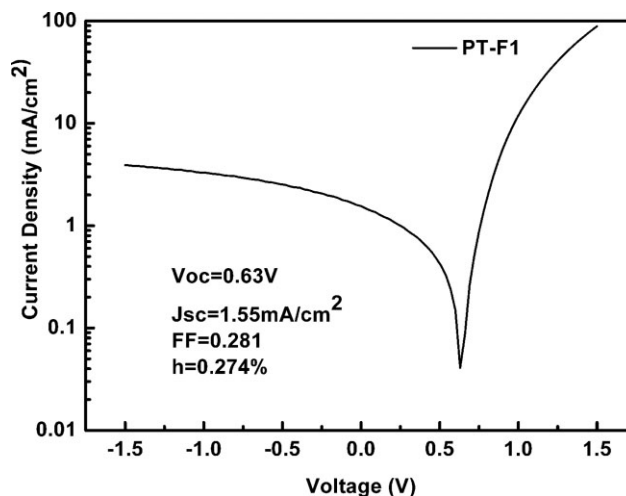


Figure 5 I - V curve of the polymer solar cell based on PT-F1 under the illumination of AM 1.5, 100 mW/cm^2 .

pendants on the side chains of the polymer **PT-F1** is poorer than that in **PT-F**.

CONCLUSIONS

The double-cable polythiophene **PT-F1** with the side chain containing fullerene end group was synthesized. The characteristic reduction peaks of C₆₀ were observed in the cyclic voltammogram of **PT-F1**, indicating that the electronic properties of C₆₀ remained in the double-cable polymers. The visible absorption of **PT-F1** is improved for some extent in comparison with that of **PT-F** reported previously. The PL quenching of the **PT-F1** dilute solution was observed, which implies that charge transfer occurs from the polymer main chain to C₆₀ on the side chains of the double-cable polymer at excited state. The power conversion efficiency of the PSC based on the single-component **PT-F1** reached 0.274%, which is a high value in the single-component PSC devices. The results indicate that these kinds of double-cable polythiophenes are promising materials in photovoltaic application.

References

1. Parmer, J. E.; Mayer, A. C.; Hardin, B. E.; Scully, S. R.; McGehee, M. D.; Heeney, M.; McCulloch, I. *Appl Phys Lett* 2008, 92, 113309.
2. Demadrille, R.; Delbosq, N.; Kervella, Y.; Firon, M.; Bettignies, D. R.; Billon, M.; Rannous, P.; Rronj, A. *J Mater Chem* 2007, 17, 4661.
3. Zhao, C. C.; Chen, X. H.; Zhang, Y.; Kitng, M. *J Polym Sci Part A: Polym Chem* 2008, 46, 2680.
4. Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromberz, T.; Hummelen, J. C. *Appl Phys Lett* 2001, 78, 841.
5. Brabec, C. J.; Shaheen, S. E.; Winder, C.; Sariciftci, N. S.; Denk, P. *Appl Phys Lett* 2002, 80, 1288.
6. Roman, L. S.; Andersson, M. R.; Yohannes, T.; Inganas, O. *Adv Mater* 1997, 9, 1164.
7. Cravino, A.; Sariciftci, N. S. *J Mater Chem* 2002, 12, 1931.
8. Ferraris, J. P.; Yassar, A.; Loveday, D. C.; Hmyene, M. *Opt Mater* 1998, 9, 34.
9. Ramos, A. M.; Rispens, M. T.; Van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J. *J Am Chem Soc* 2001, 123, 6714.
10. Ramos, A. M.; Rispens, M. T.; Hummelen, J. C.; Janssen, R. A. J. *Synth Met* 2001, 119, 171.
11. Zhang, F.; Svensson, M.; Andersson, M. R.; Maggini, M.; Bucella, S.; Menna, E.; Inganas, O. *Adv Mater* 2001, 13, 1871.
12. Benincori, T.; Brenna, E.; Sannicola, F.; Trimarco, L.; Zotti, G.; Sozzani, P. *Angew Chem Int Ed Engl* 1996, 35, 648.
13. Cravino, A.; Zerza, G.; Maggini, M.; Bucella, S.; Svensson, M.; Andersson, M.; Neugebauer, H.; Sariciftci, N. S. *Chem Commun* 2000, 24, 2487.
14. Cravino, A.; Zerza, G.; Neugebauer, H.; Maggini, M.; Bucella, S.; Svensson, M.; Andersson, M. R.; Brabec, C. J.; Sariciftci, N. S. *J Phys Chem B* 2002, 106, 70.
15. Kraabel, B. D.; Mcbranc, H.; Sariciftci, N. S.; Moses, D.; Heeger, A. *J Phys Rev B* 1994, 50, 18543.
16. Yamashiro, T.; Aso, Y.; Otsubo, T.; Tang, H.; Harima, Y.; Yamashita, K. *Chem Lett* 1999, 443.
17. Hirayama, D.; Yamashiro, T.; Takimiya, K.; Aso, Y.; Otsubo, T.; Norieda, H.; Imahori, H.; Sakata, Y. *Chem Lett* 2000, 570.
18. Van Hal, P. A.; Knol, J.; Langeveld-Voss, B. M. W.; Meskers, S. C. J.; Hummelen, J. C.; Janssen, R. A. J. *J Phys Chem A* 2000, 104, 5974.
19. Hirayama, D.; Yamashiro, T.; Takimiya, K.; Aso, Y.; Otsubo, T.; Norieda, H.; Imahori, H.; Sakata, Y. *J Am Chem Soc* 2002, 124, 532.
20. Negishi, N.; Tajunuta, K.; Aso, Y.; Ostubo, T.; Harima, Y. *Chem Lett* 2004, 33, 654.
21. Negishi, N.; Tajunuta, K.; Aso, Y.; Ostubo, T.; Harima, Y. *Synth Met* 2005, 152, 125.
22. Yasujiro, M.; Mitsuharu, S.; Koichi, K. *Org Biomol Chem* 2003, 1, 2624.
23. Tetsuya, Y.; Yasujiro, M.; Koichi, K.; Kazuaki, F.; Masao, M.; Norihiko, M.; Takeshi, Y.; Shizuo, F. *Org Lett* 2004, 6, 4865.
24. Ikemoto, J.; Tajunutam, K.; Aso, Y.; Otsubo, T.; Fujitsuka, M.; Ito, O. *Org Lett* 2002, 4, 309.
25. Peeters, P. A.; Van Hal, J. K.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. *J Phys Chem B* 2000, 104, 10174.
26. Nierengarten, J. F. *Sol Energy Mater Sol Cell* 2004, 83, 187.
27. Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F.; Liu, S. G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouall, I.; Krasnikov, V.; Hadziioannou, G. *J Am Chem Soc* 2000, 122, 7467.
28. Guldi, D. M.; Luo, C.; Swartz, A.; Gomez, R.; Segura, J. L.; Martin, N.; Brabec, C.; Sariciftci, N. S. *J Org Chem* 2002, 67, 1141.
29. Beer, E.; Feuerer, M.; Knorr, A.; Mirlach, A.; Daub, J. *Angew Chem Int Ed Engl* 1994, 33, 1087.
30. Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I.; Heeger, A. J.; Stueli, G.; Wudl, F. *Appl Phys Lett* 1993, 62, 585.
31. Cravino, A.; Zerza, G.; Maggini, M.; Bucella, S.; Svensson, M.; Andersson, M. R.; Neugebauer, H.; Brabec, C. J.; Sariciftci, N. S. *Monatsh Chem* 2003, 134, 519.
32. Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv Funct Mater* 2005, 15, 1617.
33. Reyes, M.; Kim, K.; Carroll, D. L. *Appl Phys Lett* 2005, 87, 083506.
34. Tan, Z. A.; Hou, J. H.; He, Y. J.; Zhou, E. J.; Yang, C. H.; Li, Y. F. *Macromolecules* 2007, 40, 1868.
35. Hou, J. H.; Yang, C. H.; Qiao, J.; Li, Y. F. *Synth Met* 2005, 150, 297.
36. Hou, J. H.; Huo, L. J.; He, C.; Yang, C. H.; Li, Y. F. *Macromolecules* 2006, 39, 594.
37. Fan, L. Z.; Li, Y. F.; Zheng, D. G.; Xu, J. H.; Li, Y. L.; Zhu, D. B. *Fullerene Sci Technol* 1998, 6, 963.