Synthesis and Photovoltaic Properties of a Donor−Acceptor Double-Cable Polythiophene with High Content of C_{60} Pendant

Zhan'ao Tan,[†,‡] Jianhui Hou,[†,‡] Youjun He,[†] Erjun Zhou,[†,‡] Chunhe Yang,[†] and Yongfang Li*[,†]

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100080, China, and Graduate University of Chinese Academy of Sciences, Beijing 100039, China

Received January 8, 2007; Revised Manuscript Received January 19, 2007

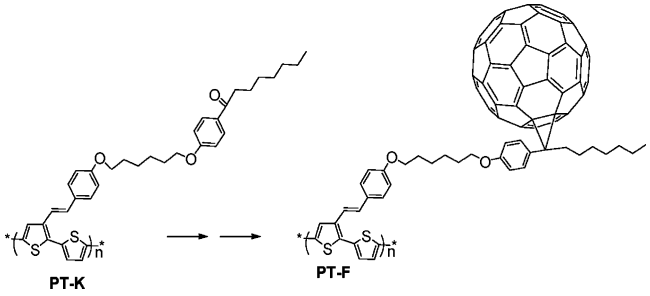
ABSTRACT: A new soluble donor−acceptor (D-A) double-cable polythiophene with higher content of C_{60} pendant, PT-F, was synthesized. The photophysical, electrochemical, and photovoltaic properties of PT-F were investigated and compared with its control polymer PT-K without C_{60} on its side chain. The polymer PT-F exhibited the characteristic reduction peaks of C_{60} at −0.783, −1.187, and −1.651 V vs Ag/Ag^+, which indicates that the electronic properties of C_{60} remained in the double-cable polymer. In comparison with PT-K, the onset oxidation potential of PT-F was increased from 0.2 to 0.3 V vs Ag/Ag^+, which could be ascribed to the steric hindrance of the big fullerene side chain. The results of the absorption and photoluminescent spectra indicate that there is no interaction at ground state between polythiophene main chains and C_{60} on the side chains, but there is strong interaction between them at excited state. The maximum power conversion efficiency of the polymer solar cell based on PT-F reached 0.52% under AM 1.5, 100 mW/cm^2, which is 5 times higher in comparison with that (0.10%) of the device based on PT-K blended with 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C-61 under the same experimental conditions. The efficiency of 0.52% is the highest value for the PSCs based on the double-cable polymers reported in the literature until now.

1. Introduction

Polymer solar cell (PSC) is a promising approach to inexpensive solar energy conversion.[1−5] The main configuration characteristic of the PSCs is the bulk heterojunction structure,[2] where the photoactive layer of the devices consists of an interpenetrating network of a π-conjugated polymer donor and a soluble fullerene acceptor. However, one of the main problems of the system is the phase separation between the polymer donor and the fullerene acceptor, which influences negatively the photoinduced charge separation and the charge transportation in the blend film and thus reduces the efficiency of the devices.[6−8] To solve this problem, the donor−acceptor (D-A) double-cable polymers were proposed.[7−13] The "double-cable" structure guarantees a homogeneous distribution of the donor/acceptor domains, and the interface between the donor and acceptor could be maximized. However, at present, the power conversion efficiency (PCE) of the devices based on the double-cable polymers was rather low in comparison with that of the devices based on a bulk heterojunction structure. A possible reason for the low efficiency is that the fullerene content in the double-cable polymers is below the percolation threshold for the formation of donor network, thus limiting the transportation of electrons.[8,13]

In order to improve the photovoltaic property of the double-cable polymers, we designed and synthesized a new double-cable polymer PT-F (see Scheme 1) with higher fullerene content and good solubility in this work. Considering polythiophenes (PTs) are good photovoltaic polymers,[3−5] we select PT as main chain of the double-cable polymer. The phenylene−vinylene side chain is selected to increase the conjugation of the polymer. We choose the alkylphenylene group attaching to the C_{60} molecule (like the substituent of 1-(3-methoxycarbonyl)-propyl-1-phenyl-[6,6]-C-61 (PCBM)) to increase the solubility of the polymer. The nonconjugated alkoxyl spacer linking the backbone and C_{60} is to avoid ground-state interaction[13] between the donor of the PT main chain and the acceptor of the C_{60} groups.

Scheme 1. Molecular Structure of the Soluble Double-Cable Polythiophene PT-F and Its Control Polymer PT-K without C_{60} End Group



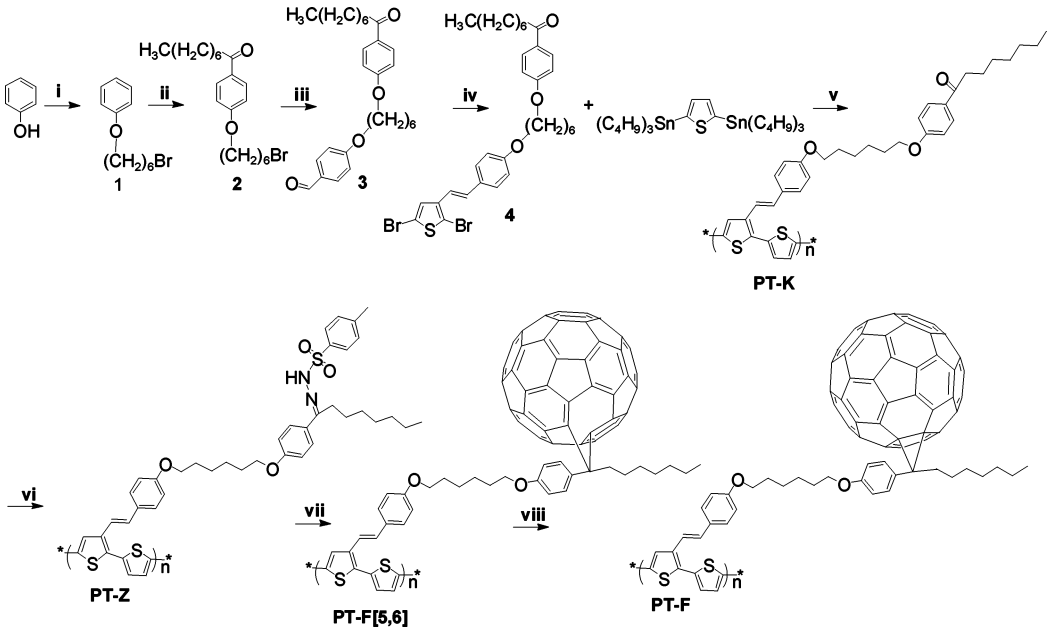
2. Results and Discussion

2.1. Synthesis and Characterization of the Polymers. The synthesis route of the double-cable polymer PT-F is shown in Scheme 2. The molecular structure of the three polymers was characterized by ^{1}H NMR and FTIR analysis. Figure 1 shows the ^{1}H NMR spectra of the three polymers: PT-K, PT-Z, and the double-cable polymer PT-F. For PT-K (see Figure 1a), there is a peak at δ 2.90 ppm for the hydrogen atoms at position 7, while for PT-Z (Figure 1b) the δ 2.90 ppm signal disappeared but a new peak at δ 2.45 ppm appeared, which is ascribed to the hydrogen atoms on position 15. Additionally, the peak at δ 2.56 ppm in Figure 1b could be attributed to the hydrogen on position 14. By FT-IR spectra analysis, as shown in Figure 2,

* Corresponding author: e-mail liyf@iccas.ac.cn, Fax 86-10-62559373.
† Institute of Chemistry, Chinese Academy of Sciences.
‡ Graduate University of Chinese Academy of Science.

10.1021/ma070052+ CCC: $37.00
Published on Web 02/17/2007

Scheme 2. Synthesis Route of the Double-Cable Polymer PT-F[a]



[a] (i) $Br(CH_2)_6Br$, KOH, H_2O, reflux for 12 h; (ii) capryl chloride, $AlCl_3$, CH_2Cl_2, ambient temperature, overnight; (iii) 4-hydroxybenzaldehyde, K_2CO_3, DMF, 80 °C, 6h; (iv) 2,5-dibromo-3-bromomethylthiophene, $P(OC_2H_5)_3$, 160 °C for 2 h, then compound **3**, CH_3ONa, DMF, cool water bath, 30 min; (v) thiophene, *n*-butyllithium, THF reflux for 2 h, then $Sn(C_4H_9)_3Cl$, ambient temperature for 12 h; (vi) compound **4**, 2,5-bis(tributylstannyl)thiophene, $Pd(PPh_3)_4$, toluene, argon, reflux for 12 h; (vii) PT-K, *p*-tosylhydrazine, trace mount of HCl, THF, reflux for 6 h; (viii) PT-Z, CH_3ONa, pyridine, stirred for 15 min, then C_{60} in *o*-dichlorobenzene, reflux for 24 h argon.

PT-K exhibited a clear peak at 1675 cm^{-1} for $\upsilon_{C=O}$ while PT-Z had no signal at that position and instead appeared a new peak of υ_{NH} at 3213 cm^{-1}. The changes of ^1H NMR and FT-IR spectra give clear evidence of the polymers PT-K and PT-Z.

The molecular structure of the double-cable polymer PT-F was also confirmed by the ^1H NMR (Figure 1c), FTIR (Figure 2), and elemental analysis. In Figure 2, PT-F shows four characteristic peaks of C_{60}[14] at 523, 574, 1182, and 1426 cm^{-1}.

2.2. Electrochemical Properties. Electrochemical cyclic voltammetry was often utilized to measure the redox properties and electronic energy levels of the conjugated polymers.[15,16] Figure 3 shows the cyclic voltammograms of the PT-K and PT-F films on Pt electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution, where PT-K is a control polymer without C_{60} end group on its side chains (see Scheme 1). PT-K exhibited similar redox behavior as the polythiophene derivatives with the phenylene−vinylene conjugated side chain.[17] After being substituted with fullerene, the polymer PT-F exhibited the characteristic reduction peaks of C_{60} at −0.783, −1.187, and −1.651 V vs Ag/Ag^+. This indicates that the electronic properties of C_{60} remained[18] after it was connected to the polymer. In comparison with PT-K, the onset oxidation potential of PT-F was increased from 0.2 to 0.3 V. Obviously, the oxidation peak was from the oxidation of the polymer main chain. The increase of the onset oxidation potential could be ascribed to the big steric hindrance of the fullerene on the side chain of PT-F, which could result in the distortion of the polymer main chain, so that the oxidation potential of the polymer increased.

2.2. Absorption and PL Spectra. Figure 4a shows absorption spectra of the PT-K and PT-F solutions in chlorobenzene. PT-K exhibits similar absorption spectrum as the phenylene−vinylene substituted polythiophenes.[17] The absorption spectrum of the double-cable polymer PT-F solution is very similar to that of the blend solution of PT-K and PCBM (see Figure 4a) and could be thought as an addition of the absorption spectra of the PT main chain and C_{60},[7] indicating that the PT main chain and C_{60} in PT-F are not in one conjugated system and there is no ground state interaction between the PT main chain and C_{60} in PT-F. Figure 4b shows the film absorption spectra of PT-K, PT-F, and PT-K blended with PCBM. The absorption bands in solid state are broadened and red-shifted by about 30 nm compared to the solution spectra. This is mostly due to the more planar conformation resulting from π-stacking/aggregation in solid state. In addition, it can be seen from Figure 4b that the absorption band edge of PT-F is close to that of PT-K, which indicates that the C_{60} groups on the side chains have little effect on the band gap of the PT main chain.

Figure 5a shows the photoluminescence (PL) spectra of PT-K, PT-F dilute solutions, and the dilute blend solution of PT-K and PCBM (1:1; mol/mol). The PL spectrum of the PT main chains in the dilute PT-F solution was greatly quenched by the fullerene on its side chains due to the photoinduced electron transfer from PT unit to C_{60} moiety, while the PL intensity of the dilute blend solution of PT-K and PCBM was only slightly decreased in comparison with that of the PT-K solution, indicating that the charge transfer from PT-K to PCBM in the dilute blend solution is difficult. The PL quenching in the PT-F dilute solution confirms unambiguously the covalent linkage of the C_{60} moieties to the polymer backbone in PT-F. Figure 5b shows the film PL spectra of PT-K, PT-F, and PT-K blended with PCBM. It shows that the PL of PT-F was entirely quenched and that of PT-K blended with PCBM was also dramatically quenched. This result indicates that in PT-F system the charge transfer from the photoexcited conjugated backbone to the fullerene was more effective than that in the PT-K blended with the PCBM system.[19,20]

2.3. Surface Morphology of Polymer/PCBM Blend Films. The height image of the PT-F film (see Figure 6a) shows clearly that the surface of the polymer film is very smooth (its rms roughness is only 1.459 nm), and there is no aggregation formed, while the rms roughness of the blend film of PT-K and PCBM is 3.238 nm (see Figure 6b), which is much larger than that of the PT-F film. The small feature size in the PT-F film would facilitate exciton separation and thus yield higher charge

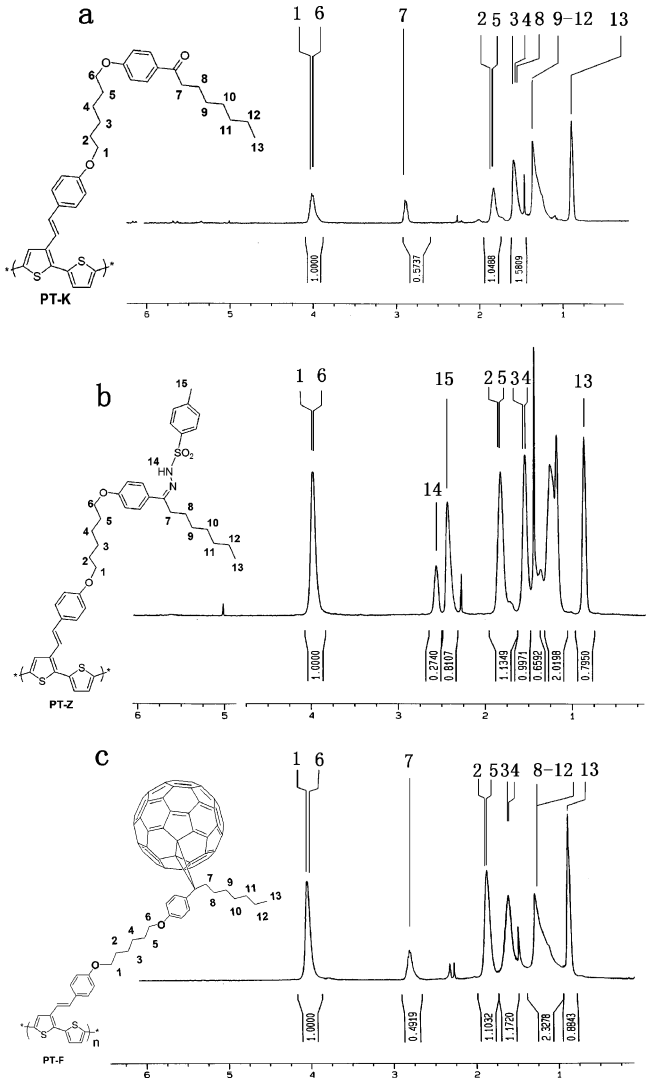


Figure 1. ^{1}H NMR spectra of the polymers (a) PT-K, (b) PT-Z, and (c) PT-F.

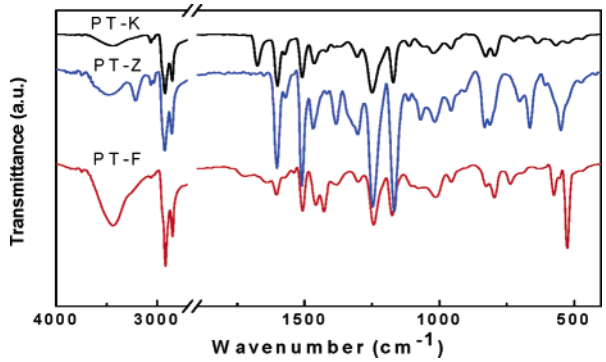


Figure 2. FT-IR spectra of the polymers PT-K, PT-Z, and PT-F.

separation efficiency, since the exciton diffusion length in polymer materials is typically small.[21,22] The results indicate that the interpenetrating network in PT-F film was greatly improved in comparison with that of the blend film of PT-K and PCBM.

2.4. Photovoltaic Properties. 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). The photosensitive layer was made of PT-F or PT-K blended with PCBM (1:1, mol/mol). Figure 7 shows the $I-V$ curves of the

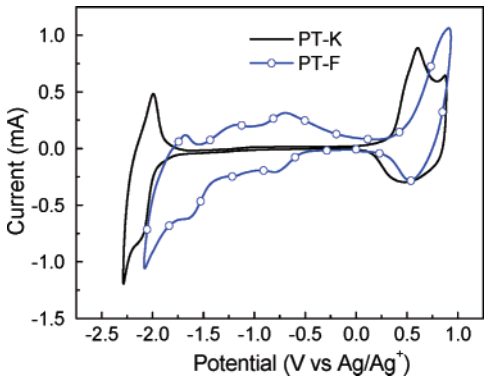


Figure 3. Cyclic voltammograms of the PT-K and PT-F films on platinum electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution with a scan rate of 100 mV/s.

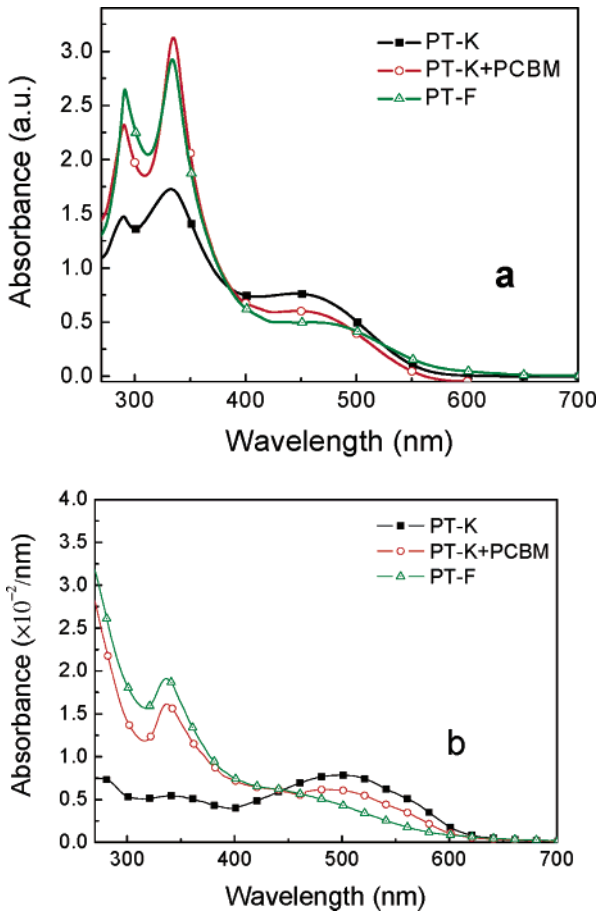


Figure 4. Absorption spectra of PT-K, PT-F, and PT-K blended with PCBM (1:1, mol/mol): (a) dilute solutions in chlorobenzene (5×10^{-5} mol/L) and (b) solid film.

PSC based on PT-F and the device based on PT-K blended with PCBM, and the photovoltaic parameters are given in the inset of the figure. It can be seen that the short-circuit current (J_{sc}) of the PSC based on PT-F reached 2.41 mA/cm^2, which is 4 times higher than that of the device based on PT-K blended with PCBM. The improvement of J_{sc} based on PT-F could be ascribed to the efficiently PL quenching (see Figure 5a,b) and the uniform morphology (see Figure 6a). The lower J_{sc} based on the blend of PT-K with PCBM might be due to the bigger insulating side chain of PT-K which obstructed the charge separation and transportation between PT-K and PCBM.[23,24] The open-circuit voltage (V_{oc}) of PT-F is 0.75 V, 0.12 V higher than that based on PT-K blended with PCBM. The increase of the

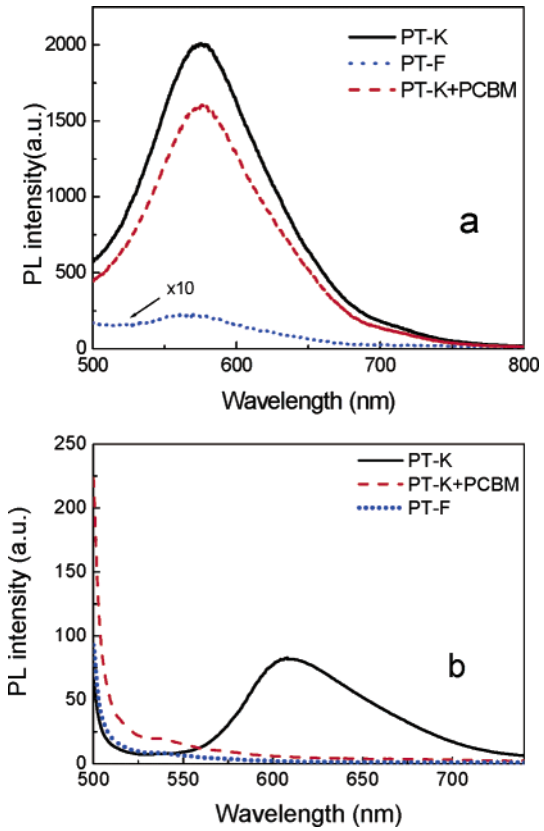


Figure 5. Photoluminescence spectra of PT-K, PT-F, and PT-K blended with PCBM (1:1, mol/mol): (a) dilute solutions in chlorobenzene (5×10^{-5} mol/L) and (b) solid film.

V_{oc} based on PT-F may result from the lower HOMO levels as shown in Figure 3, since V_{oc} is related to the energy difference between the LUMO of the acceptor (PCBM) and the HOMO of the donor (conjugated polymer).[25−27] Under the illumination of AM 1.5, 100 mW/cm^2, the power conversion efficiency of the device based on PT-F reached 0.52%, which is more than 5 times higher than that of the device based on the PT-K blend with PCBM. Among the D-A double-cable polymers, this is the highest value reported in literature to the best of our knowledge.

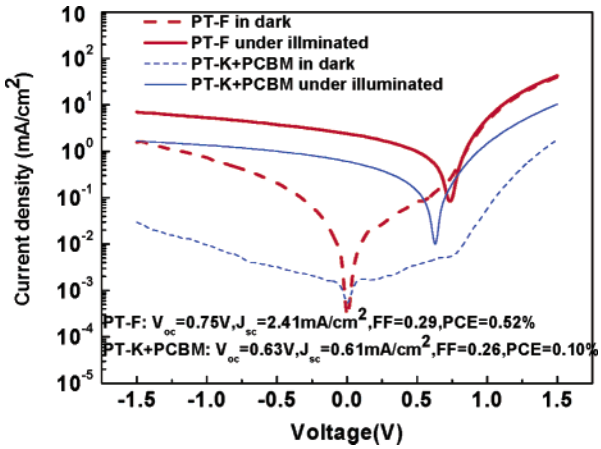


Figure 7. *I*−*V* curves of the polymer solar cells based on PT-F and PT-K blended with PCBM in dark and under the illumination of AM1.5, 100 mW/cm^2.

3. Conclusion

A soluble D-A double-cable polythiophene with high content of C_{60} pendant, PT-F, was synthesized and characterized. The characteristic reduction peaks of C_{60} were observed in the cyclic voltammogram of PT-F, indicating that the electronic properties of C_{60} remained in the double-cable polymer. In comparison

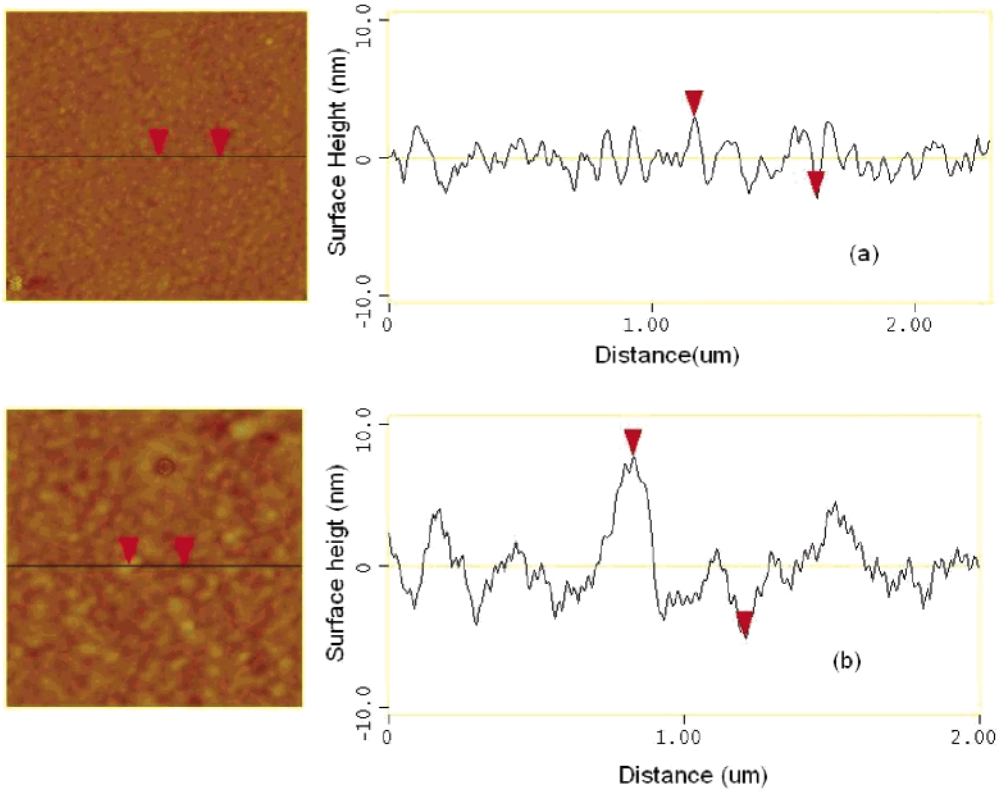


Figure 6. Atomic force microscopy (AFM) images of (a) the surface of PT-F film and (b) the surface of the blend film of PT-K and PCBM. The films were spin-coated from chlorobenzene solutions.

with the control polymer PT-K without C_{60} on its side chains, the onset oxidation potential of PT-F was increased from 0.2 to 0.3 V vs Ag/Ag^+, which could be ascribed to the steric hindrance of the big fullerene side chain of PT-F. The results of the absorption and photoluminescent spectra indicate that there is no interaction at ground state between polythiophene main chains and C_{60} on the side chains, but there is strong interaction between them at excited state. The photovoltaic properties of the polymer were investigated on the basis of the device structure of ITO/PEDOT:PSS/PT-F/Ca/Al. The open-circuit voltage (V_{oc}) of the polymer solar cell (PSC) is 0.75 V, 0.12 V higher than that of the device based on PT-K blended with PCBM. Under the illumination of AM 1.5, 100 mW/cm^2, the power conversion efficiency of the device reached 0.52%, which is more than 5 times higher than that of the device based on PT-K blended with PCBM. The results indicate that the D-A double-cable polymer PT-F is a promising material for photovoltaic applications.

4. Experimental Section

4.1. Materials and Instruments. 2,5-Dibromo-3-bromomethylthiophene was synthesized as reported.[17] All other regents were common commercial level and used as received. ^{1}H NMR spectra were measured on a Bruker DMX-300 spectrometer. Elemental analysis was carried out on a Flash EA 1112 elemental analyzer. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Waters 515 HPLC pump, a Waters 2414 differential refracometer, 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 (Bu_4NPF_6) acetonitrile solution. The atomic force microscopy (AFM) images were taken using a Digital Instruments Nanoscope III (DI, USA) operating in tapping mode. All the samples were prepared under the same conditions as that used in photovoltaic devices.

4.2. Synthesis. The synthetic route of the double-cable polymer PT-F is shown in Scheme 1. The detailed synthetic procedures are as follows:

1-(6-Bromohexyloxy)benzene, 1. Phenol 9.4 g (0.1 mol) and water (50 mL) were put into a flask, and KOH 5.6 g (0.1 mol) was added. After the phenol was dissolved, 96.8 g (0.4 mol) of 1,6-dibromohexane was added 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 20.6 g (80 mmol, yield 80%) of colorless 1-(6-bromohexyloxy)benzene.

GC-Ms: $m/z = 256$. ^{1}H NMR (δ/ppm, $CDCl_3$): 7.21 (t, 2H), 6.92 (d, 1H), 6.75 (d, 2H), 3.85 (t, 2H), 3.15 (t, 2H), 1.81 (quintuple, 2H), 1.72 (quintuple, 2H), 1.33 (m, 4H). Calculated for $C_{15}H_{22}O_2$: C = 56.04; H = 6.66; found: C = 56.17; H = 6.56.

1-Octanoyl-4-(6-bromohexyloxy)benzene, 2. Anhydrous aluminum trichloride (12 g, 90 mmol) was added to 50 mL of dichloromethane, and then capryl chloride (8.88 g, 60 mmol) was added slowly. The mixture was stirred at ambient temperature for 1 h. In an ice−water bath, 1-(6-bromohexyloxy)benzene was added dropwise below 5 °C. After the addition of compound **1**, the reactant was stirred overnight. Then the mixture was poured into 250 g of ice, and a white solid was obtained. After recrystallization from methanol, a white solid of 1-octanoyl-4-(6-bromohexyloxy)-benzene was obtained (14.4 g, yield 63%).

GC-Ms: $m/z = 382$. ^{1}H NMR (δ/ppm, $CDCl_3$): 7.92 (d, 2H), 6.96 (d, 2H), 4.02 (t, 2H), 3.42 (t, 2H), 2.89 (t, 2H), 1.91 (m, 2H), 1.84 (m, 2H), 1.73 (m, 2H), 1.51 (m, 6H), 1.30−1.25 (m, 6H), 0.85 (t, 3H). Calculated for $C_{20}H_{31}BrO_2$: C = 62.66; H = 8.15; found: C = 62.50; H = 8.16.

4-(6-(4-Octanoylphenoxy)hexyloxy)benzaldehyde, 3. Compound **3** (11.46 g, 30 mmol), 4-hydroxybenzaldehyde (3.66 g, 30 mmol), and K_2CO_3 (4.14 g, 30 mmol) were put into a 250 mL flask with 50 mL of *N*,*N*-dimethylformamide. The mixture was stirred for 6 h at 80 °C. Then the reactant was poured into 200 mL of cool water and extracted with ether three times. The combined organic layer was washed with water and then dried over anhydrous $MgSO_4$, filtered, and concentrated. The product of compound **3** was purified by recrystallization from methanol and obtained as a white solid (8.54 g, yield 67%).

GC-Ms: $m/z = 424$. ^{1}H NMR (δ/ppm, $CDCl_3$): 9.87 (s, 1H), 7.93 (d, 2H), 7.81 (d, 2H), 6.98 (d, 2H), 6.90 (d,1H), 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, 8H), 0.87 (t, 3H). Calculated for $C_{15}H_{22}O_2$: C = 76.38; H = 8.55; found: C = 76.30; H = 8.56.

3-(4-(6-(4-Octanoylphenoxy)hexyloxy)styryl)-2,5-dibromothiophene, 4. 2,5-Dibromo-3-bromomethylthiophene (3.35 g, 10 mmol) and phosphorus acid triethyl ester (1.66 g, 10 mmol) 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** (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 recrystallization from methanol and obtained as a white solid (5.04 g, yield 76%).

GC-Ms: $m/z = 660$. ^{1}H NMR (δ/ppm, $CDCl_3$): 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, 8H), 0.88 (t, 3H). Calculated for $C_{32}H_{38}Br_2O_3S$: C = 58.01; H = 5.78; Br = 24.12; O = 7.24; S = 4.84; found: C = 58.10; H = 5.71; Br = 24.20; O = 7.08; S = 4.79.

2,5-Bis(tributylstannyl)thiophene. Thiophene (8.4 g, 0.10 mol) was dissolved in 60 mL of THF in a well-dried flask under the protection of nitrogen. *n*-Butyllithium (76 mL, 0.22 mol, 2.88 M 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 (70 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. After distillation under vacuum (0.1 mmHg/190 °C), 35 g (0.053 mol, yield 53%) of 2,5-bis(tributylstannyl)thiophene was obtained.

Purity (by GC) >96%. GC-Ms: $m/z = 664$. ^{1}H NMR (δ/ppm, $CDCl_3$): 7.34 (s, 2H), 1.60 (m, 12H), 1.39 (m, 12H), 1.09 (m, 12H), 0.91 (t, 18H).

Synthesis of the Polymer PT-K. 1.0 mmol of compound **4** was put into a three-neck flask. Then, 15 mL of degassed toluene was added under the protection of argon. The solution was flushed with argon for 10 min, and then 50 mg of $Pd(PPh_3)_4$ and 1.0 mmol of 2,5-bis(tributylstannyl)thiophene were added. After another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. Then the reactant was cooled to room temperature, and the polymer was precipitated by addition of 50 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation as a solid. The solid was dried under vacuum for 1 day. The yield of polymerization reaction was 280 mg (~50%).

Calculated for $C_{36}H_{40}O_3S_2$: C = 73.93; H = 6.89; O = 8.21; S = 10.97; found: C = 73.38; H = 6.78; O = 8.82; S = 10.23.

Synthesis of the Polymer PT-Z. 200 mg of PT-K was dissolved in 50 mL of THF with excessive amount of *p*-tosylhydrazine (0.2 g), and 3 drops of concentrated hydrochloric acid was added in.

The solution was refluxed for 6 h. Then the polymer was precipitated by addition of 100 mL of methanol. The precipitation was washed with methanol in a Soxhlet thimble for 12 h. The red residue that was collected and dried under vacuum gave out 230 mg of PT-Z (yield 91%).

The structure of PT-Z was proved by the FT-IR spectrum in Figure 2. Calculated for $C_{43}H_{48}N_2O_4S_3$: C = 68.58; H = 6.42; N = 3.72; O = 8.50; S = 12.77; found: C = 69.48; H = 6.72; N = 3.99; O = 8.98; S = 12.52.

Synthesis of the Polymer PT-F. A similar procedure for the synthesis of PCBM as reported by Wudl[28] was used. The polymer PF-Z (200 mg, ~0.28 mmol) was dissolved in 10 mL of dry pyridine in a dried flask. Then, $NaOCH_3$ (18 mg, 0.33 mmol) was added, and the mixture was stirred for 15 min. Then a solution of 360 mg (0.5 mmol) of C_{60} in 20 mL of 1,2-dichlorobenzene was added. The reactant was stirred for 24 h. The reaction mixture was concentrated to 20 mL, and 50 mL of hexane was added. The precipitation was subjected to Soxhlet extraction with methanol for 12 h, hexane for 48 h, THF for 24 h, and chlorobenzene for 24 h. The unreacted C_{60} was recovered from hexane fraction. The solid recovered from THF fraction and chlorobenzene fraction were the polymers with different content of C_{60}. The fraction from THF was about 80 mg, and the carbon content of it was 82.70%; the fraction from chlorobenzene faction was about 120 mg, and the carbon content of it was 89.51%. By analysis with carbon content, the mole ratio of C_{60} to the polymer repeat units from THF fraction was about 0.4:1; that of fraction from chlorobenzene was about 1:1. The fraction from chlorobenzene was collected by rotary evaporation as solid, and then, the solid was dissolved into dichlorobenzene and heated to reflux for 4 h. After removing solvent, the solid was dried under vacuum for 1 day.

Calculated for $C_{96}H_{40}O_2S_2$: C = 89.42; H = 3.13; S = 4.97; found: C = 89.91; H = 2.98; S = 4.43. By elemental analysis, the content of carbon in PT-F was 89.42%, which is close to the theoretical value, 89.91%. Therefore, we concluded that nearly each repeated units of PT-F was substituted by one C_{60} molecule.

The weight-average molecular weights (M_w) of PT-K and PT-Z were 1.5×10^4 and 1.7×10^4 with the polydispersity index (PDI) of 1.9 and 2.2, respectively. The molecular weight of PT-F 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 PT-K and PT-Z, the M_w of PT-F should be in the range of 20K−40K because C_{60} is connected with the polymer side chains without interruption of the polymer main chain during the synthesis of PT-F.

4.3. Fabrication and Characterization of Polymer Solar Cells. Polymer solar cells were fabricated with the structure of ITO/PEDOT:PSS/active layer/Ca/Al. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS (Bayer) which was spin-cast from a PEDOT:PSS aqueous solution on the ITO substrate, and the thickness of PEDOT: PSS is about 30 nm. The photosensitive layer, PT-F or PT-K blended with PCBM (1:1 mol/mol), was prepared by spin-coating their chlorobenzene solution on the ITO/PEDOT:PSS electrode and dried at 80 °C for 30 min. The thickness of the photosensitive layer was controlled to ca. 65 nm by adjusting the rotating speed of the spin-coating and was measured on an Ambios Tech. XP-2 profilometer. Then the metal cathode, which is made up of Ca and Al, was deposited on the polymer layer by vacuum evaporation under 5×10^{-5} Pa. The Ca layer was deposited by a speed of 0.03−0.05 nm/s, the thickness of which is 10 nm. Then, the Al layer was deposited by a speed of 0.1−0.3 nm/s, the thickness of which is 150 nm. The effective area of one cell is 4 mm^2. Surface roughness of the active layer was determined by AFM. The current−voltage ($I-V$) measurement of the devices was conducted on a computer-controlled Keithley 236 source measure unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm^2.

Acknowledgment. This work was supported by NSFC (No. 20474069, 20421101, 20574078, and 50633050) and The Ministry of Science and Technology of China (973 Project, No. 2002CB613404 and 863 Project, No. 2006AA03Z220).

References and Notes

(1) Sacriciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.

(2) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(3) (a) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617. (b) Kim, J. Y.; Kim, S. H.; Lee, H. H.; Lee, K.; Ma, W.; Gong, X.; Heeger, A. J. *Adv. Mater.* **2006**, *18*, 572.

(4) (a) Shao, Y.; Yang, Y. *Adv. Mater.* **2005**, *17*, 2841. (b) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.

(5) Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. *J. Am. Chem. Soc.* **2006**, *128*, 4911.

(6) Sariciftci, N. S.; Heeger, A. J. *Synth. Met.* **1995**, *70*, 1349.

(7) (a) Benincori, T.; Brenna, E.; Sannicolo, F.; Trimarco, L.; Zotti, G.; Sozzani, P. *Angew. Chem., Int. Ed.*, **1996**, *35*, 648. (b) Cravino, A.; Sariciftci, N. S. *J. Mater. Chem.* **2002**, *12*, 1931.

(8) Nierengarten, J. F.; Ecker, J. F.; Nicoud, J. F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617.

(9) Marcos Ramos, A.; Rispens, M. T.; Van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2001**, *123*, 6714.

(10) Zhang, F.; Svensson, M.; Andersson, M. R.; Maggini, M.; Bucella, S.; Menna, E.; Inganas, O. *Adv. Mater.* **2001**, *13*, 1871.

(11) Roncali, J. *Chem. Soc. Rev.* **2005**, *34*, 483.

(12) Xiao, S. Q.; Wang, S.; Fang, H. J.; Li, Y. L.; Shi, Z. Q.; Du, C. M.; Zhu, D. B. *Macromol. Rapid Commun.* **2001**, *22*, 1313.

(13) Yang, C. H.; Li, H. M.; Sun, Q. J.; Qiao, J.; Li, Y. L.; Li, Y. F.; Zhu, D. B. *Sol. Energy Mater. Sol. Cells* **2005**, *85*, 241.

(14) Krätchmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature (London)* **1990**, *347*, 354.

(15) Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243.

(16) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800.

(17) Hou, J. H.; Huo, L. J.; He, C.; Yang, C. H.; Li, Y. F. *Macromolecules* **2006**, *39*, 594.

(18) Fan, L. Z.; Li, Y. F.; Li, F. Y.; Zheng, D. G.; Xu, J. H.; Li, Y. L.; Zhu, D. B. *Fullerene Sci. Technol.* **1998**, *6*, 963.

(19) Peeters, E.; Van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *122*, 10174.

(20) 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*, 5964.

(21) Hoppe, H.; Niggemann, M.; Winder, C.; Kraut, J.; Hiesgen, R.; Hinsch, A.; Meissner, D.; Sariciftci, N. S. *Adv. Funct. Mater.* **2004**, *14*, 1005.

(22) van Duren, J. K. J.; Loos, J.; Morrisser, F.; Leewis, C. M.; Kivits, K. P. H.; van IJzendoorn, L. J.; Rispens, M. T.; Hummelen, J. C.; Janssen, R. A. J. *Adv. Funct. Mater.* **2002**, *12*, 66.

(23) Hoppe, H.; Niggemann, M.; Winder, C.; Kraut, J.; Hiegen, R.; Hinsch, A.; Meissner, D.; Sariciftci, N. S. *Adv. Funct. Mater.* **2004**, *14*, 1005.

(24) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617.

(25) Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Framherz, Th.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 374.

(26) Mihailetchi, V. D.; Blorn, P. W. M.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94*, 6849.

(27) Dyakonov, V. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 21.

(28) Wudl, F. *J. Mater. Chem.* **2002**, *12*, 1959.

MA070052+