

Effect of Carbon Chain Length in the Substituent of PCBM-like Molecules on Their Photovoltaic Properties

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A series of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM)-like fullerene derivatives with the butyl chain in PCBM changing from 3 to 7 carbon atoms, respectively (F1-F5), are designed and synthesized to investigate the relationship between photovoltaic properties and the molecular structure of fullerene derivative acceptors. F2 with a butyl chain is PCBM itself for comparison. Electrochemical, optical, electron mobility, morphology, and photovoltaic properties of the molecules are characterized, and the effect of the alkyl chain length on their properties is investigated. Although there is little difference in the absorption spectra and LUMO energy levels of F1-F5, an interesting effect of the alkyl chain length on the photovoltaic properties is observed. For the polymer solar cells (PSCs) based on P3HT as donor and F1-F5, respectively, as acceptors, the photovoltaic behavior of the P3HT/F1 and P3HT/F4 systems are similar to or a little better than that of the P3HT/PCBM device with power conversion efficiencies (PCEs) above 3.5%, while the performances of P3HT/F3 and P3HT/F5-based solar cells are poorer, with PCE values below 3.0%. The phenomenon is explained by the effect of the alkyl chain length on the absorption spectra, fluorescence quenching degree, electron mobility, and morphology of the P3HT/F1-F5 (1:1, w/w) blend films.

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1. Introduction

Polymer solar cells (PSCs) with a bulkheterojunction (BHJ) active layer in the structure have attracted great attention in recent years, because of their advantages of low cost, light weightedness, and flexibility.^[1-4] Various combinations of donor and acceptor materials have been used in the BHJ active layer of the PSCs. One of the most representative BHJ PSCs is the device based on a blend of poly(3-hexylthiophene) (P3HT) as an electron donor and a soluble C₆₀ derivative, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as an electron acceptor. The power conversion efficiency (PCE) of the PSCs based on P3HT:PCBM reached over 4% by thermal treatment,^[5a] solvent^[5b] and vapor^[6] annealing, as well as mixture solvent treatment.^[7] To further improve the PCE, new conjugated polymer donors and fullerene derivative acceptors are needed for a higher short circuit current (I_{sc}) and a higher open circuit voltage (V_{oc}). In recent

years, various new types of low bandgap polymer donors have been developed, and the PCEs of the PSCs based on these polymers reach 5%-7%.^[2,8–12]

In comparison with the significant publications on the new polymer donors, the attention on new fullerene derivative acceptors is much less. Recent reports on the new fullerene derivatives include PCBM derivatives with electron-donating groups on the phenyl ring^[13,14] or with other groups that replace the phenyl ring,^[15] a PCBM bisadduct^[16] or PCBM multi adduct,^[17] penta(organo)[60]fullerenes,^[18] silymethyl[60]fullerene,^[19] endohedral fullerenes,^[20] and other C_{60} derivatives.^[21] Unfortunately, among these new fullerene derivatives, most show poorer photovoltaic properties, and only a few show similar or a slightly better photovoltaic performance than PCBM.^[15c,16,20,21b] It should be noticed that a new fullerene derivative, an indene-C₆₀ bisadduct (ICBA), was reported recently, and the PSC based on P3HT/ICBA showed a high V_{oc} of 0.84 V and a higher PCE of 5.44%, $^{[22]}$ which is significantly improved in comparison with that of the PSCs based on P3HT/PCBM. Up to now, the most important fullerene derivative acceptors are still PC60BM and PC70BM (the corresponding PCBM derivative of C70). It is also interesting to note that a slight structural modification of PCBM can influence the



Scheme 1. Molecular structures of the five fullerene derivatives F1-F5.

photovoltaic performance significantly. Therefore, it is essential to understand the effect of the side chain structure of the fullerene derivatives on their photovoltaic properties.

Here we designed and synthesized a series of PCBM-like C_{60} derivatives, F1, F2, F3, F4, and F5 (Scheme 1), by changing the butyl carbon chain length of PCBM (F2) from 3 to 7 carbon atoms, respectively, to investigate the effect of the carbon chain length of PCBM on the physical properties and photovoltaic performance of the PCBM derivatives. Among the molecules, F2 is PCBM itself for comparison. The molecules of F1-F5 possess almost the same lowest unoccupied molecular orbital (LUMO) energy levels and absorption characteristics. But, interestingly, the PSCs based on P3HT as donor and F1-F5 as acceptor showed different photovoltaic performances depending on the PCBM derivatives. The PSCs with F1, F2, or F4 as the acceptor displayed higher photovoltaic performance with PCE above 3.5%, while those with F3 or F5 as acceptors showed a relatively lower PCE below 3.0%. In comparison with PCBM (F2), F1 with a side-chain one carbon shorter, and F4 with a side-chain two carbons longer, display similar or a slightly better photovoltaic performance than PCBM, while F3 with a side-chain one carbon longer and F5 with a sidechain three carbons longer show a poorer photovoltaic performance. The absorption and photoluminescence spectra, electron mobilities, and the morphology of the P3HT/F1-F5 blend films were analyzed to explain the phenomenon.

2. Results and Discussion

2.1. Absorption Spectra and Electrochemical Properties of the Fullerene Derivatives

Figure 1 shows the UV-vis absorption spectra of the fullerene derivatives (F1–F5) in toluene solution. The absorption spectra of F1–F5 derivatives are nearly the same: there are two absorption peaks located in 283 and 332 nm, respectively. The absorption spectra indicate that the alkyl chain length in the side chain of PCBM affects the absorption spectra very little.

The electrochemical property is one of the most important properties of fullerenes. Electronic energy levels (especially the LUMO level) of the fullerene derivatives are crucial for their application in PSCs as acceptor, which can be measured by electrochemical cyclic voltammetry. Therefore, we measured the cyclic voltammograms of F1–F5, as shown in Figure 2. It can be seen that the five cyclic voltammograms exhibit similar three reversible reduction/reoxidation processes over a negative potential range. The onset reduction potentials of F1–F5 are

-0.80, -0.80, -0.79, -0.81, and -0.80 V, respectively. The LUMO energy levels of the fullerene derivatives were calculated from the onset reduction potentials (φ_{red}) according to the following equation:^[23] $E_{LUMO} = -(\varphi_{red} + 4.71)$ (eV), where the units of φ_{red} are V vs. Ag/Ag⁺. The LUMO energy levels of F1–F5 are -3.91,



Figure 1. Absorption spectra of F1-F5 solutions in toluene.



Figure 2. Cyclic voltammograms of F1, F2, F3, F4, and F5 in a mixed solution of *ortho*-dichlorobenzene/acetonitrile (5:1, v/v) with 0.1 M Bu₄NPF₆ at 100 mV s⁻¹.



-3.91, -3.92, -3.90, and -3.91 eV, respectively. Obviously, there is little change of the LUMO energy levels of the five fullerene derivatives, which means that the influence of the alkyl chain length in the side chain of PCBM on the LUMO energy level of the molecules is very weak.

2.2. Photovoltaic Properties

The motivation for the design and synthesis of these fullerene derivatives is to look for new fullerene derivatives as acceptors for highly efficient PSCs and to investigate the effect of the side chain structure of PCBM on its photovoltaic properties. We fabricated PSCs based on P3HT/F1-F5 blend films with the structure of indium tin oxide (ITO)/poly(3,4-ethylene dioxythiophene):poly-(styrene sulfonate) (PEDOT:PSS)/P3HT:F1-F5 (1:1, w/w)/Ca/Al, where the polymer P3HT was used as the electron donor and fullerene derivatives F1-F5 were used as electron acceptors. For comparison, the experimental conditions of the PSCs are the same except for the different acceptors of F1-F5. Figure 3 shows the I-V curves of the PSCs under the illumination of AM1.5G, $100 \,\mathrm{mW \, cm^{-2}}$. The photovoltaic performance data of the PSCs, including the open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and PCE values, are summarized in Table 1 for a clear comparison. It can be seen from Table 1 that the PSCs based on P3HT/F1, P3HT/F2(PCBM), and P3HT/F4 blend films demonstrate a similar performance with PCE values of 3.7%, 3.5%, and 3.6%, respectively. While those for P3HT/F3 and P3HT/ F5-based solar cells show poorer PCEs of 2.3% and 2.8%, respectively. In comparison with the PSC with PCBM (F2) as the acceptor, the PSCs with F1 and F4 as the acceptor show similar or a slightly higher efficiency, which is higher than 3.5%, however, the PSCs with F3 and F5 as the acceptor show poorer efficiency, which is lower than 3.0%. The higher PCE of the devices with F1 and F4 as acceptor has benefited from a slightly higher I_{sc} , and the poorer PCE of the PSCs with F3 and F5 as acceptor has suffered from a lower $V_{\rm oc}$, lower FF, and a little lower $I_{\rm sc}$. We repeated the



Figure 3. I-V curves of the PSCs based on the blend of P3HT as donor and F1-F5 as acceptors (1:1, w/w) under the illumination of AM1.5G, 100 mW cm⁻².



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Table 1. Photovoltaic performance of the PSCs based on a blend of P3HT and F1–F5 (1:1, w/w) under the illumination of AM1.5G, 100 mW cm^{-2} .

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Active layer	$V_{\rm oc}$ [V]	$I_{\rm sc} [{\rm mA cm^{-2}}]$	FF [%]	PCE [%]
P3HT/F1	0.564	10.8	60.3	3.7
P3HT/F2	0.571	9.6	64.6	3.5
P3HT/F3	0.535	8.1	53.2	2.3
P3HT/F4	0.596	9.9	61.5	3.6
P3HT/F5	0.540	9.3	56.4	2.8

experiments more than 10 times, the tendency of the effect of the alkyl chain length of the PCBM-like C_{60} derivative on the photovoltaic properties is the same and reproducible.

Figure 4 shows the external quantum efficiencies (EQEs) of the PSCs based on the blend of P3HT/F1–F5 films (1:1, w/w). The EQE values of the devices are consistent with their $I_{\rm sc}$ values and the PSCs with F3 and F5 as acceptor show lower EQE values than that with PCBM (F2) as acceptor.

2.3. Optical Properties of Absorption and Photoluminescence Spectra for P3HT/F1–F5 Blend Films

The absorption spectra of P3HT and F1–F5 blend films (1:1, w/w) are shown in Figure 5a. There are three vibronic absorption shoulders for P3HT/F1–F5 blend films in visible region deriving from the contribution of the absorption for P3HT. The absorption intensities of the blend films differ in the order of P3HT/F1 > P3HT/F4 > P3HT/F2 > P3HT/F5 > P3HT/F3 which is consistent with the tendency of I_{sc} for the five PSCs based on the P3HT/F1–F5 systems. As shown in Figure 5a, the five blend films show one absorption peak at ~332 nm in ultraviolet region which is from the contribution of fullerenes derivatives F1–F5. And the P3HT/F3 and P3HT/F5, especially for P3HT/F3, show weaker absorption intensities than those of other three blend films. We find the densities of F3 and F5 are lower than those of the weak



Figure 4. EQEs of the PSCs based on the blend of P3HT/F1-F5 films (1:1, w/w).

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Figure 5. a) Absorption and b) photoluminescence spectra of P3HT/F1– F5 blend films.

absorption intensities at \sim 332 nm for P3HT/F3 and P3HT/F5 may be the relatively large size of the molecular structure of F3 and F5, which induces a the low content of F3 and F5 in the unit thickness of the blend films.

Photoluminescence (PL) quenching for the BHJ blend films results from the charge separation of excitons at the donor/ acceptor interface, and the degree of the PL quenching reflects the efficiency of the exciton charge separation which influences the I_{sc} value of the PSCs based on the blend films. In order to understand the origin of the effect of the alkyl chain length of the PCBM-like molecules F1-F5 on the photovoltaic performance of the PSCs with the molecules as acceptor, we measured the PL spectra of the P3HT/F1-F5 films, as shown in Figure 5b. All the blend films show obvious PL peaks of P3HT at ~650 nm, which indicates that the P3HT aggregates to some extent and the charge separation efficiency of the excitons in the blend films is lower than 100%.^[24] Among the five blend films, the P3HT/F3 blend film displays the highest PL intensity, which means that the degree of PL quenching of the P3HT/F3 blend film is lower than those of other blend films. Probably, the domain size of the P3HT aggregation is larger, or the electron transfer speed at the interface of P3HT/F3 is lower, in the P3HT/F3 blend film, which results in a lower PL quenching degree and lower I_{sc} of the corresponding PSC device.



Figure 6. J-V characteristics of the electron-only diodes (a) and corresponding fits to the SCLC model (b) of P3HT/F1–F5 blend films (1:1, w/w). The numbers shown in plots are the film thickness of samples.

2.4. Electron Mobility

Charge carrier mobility is one of the major concerns in designing organic photovoltaic materials and in fabricating PSCs. A high charge carrier mobility is preferred for efficient transportation and photocurrent collection of the photo-induced charge carriers. We measured the electron mobilities of P3HT/F1–F5 blend films by the space-charge limited current (SCLC) method^[25] with the electron-only devices, to investigate the effect of the alkyl chain length of F1–F5 on the electron mobility. For the electron-only devices, SCLC is described by:

$$J = \frac{8}{9} \varepsilon_r \varepsilon_0 \mu_e \frac{V^2}{L^3} \tag{1}$$

where *J* is the current density, ε_r is the dielectric constant of the fullerene derivatives F1–F5, ε_0 is the permittivity of the vacuum, *L* is the thickness of the blend film, $V = V_{appl} - V_{bi}$, V_{appl} is the





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Figure 7. AFM (5 μ m \times 5 μ m) topography images of a) P3HT/F1, b) P3HT/F2, c) P3HT/F3, d) P3HT/F4, and e) P3HT/F5 blend films.





Scheme 2. Synthetic route of the fullerene derivatives: i) Methanol, sulfuric acid, reflux for 4–8 h; ii) 4-methylbenzenesulfonohydrazide, methanol, reflux for 4–8 h; iii) C₆₀, pyridine, NaOMe, *ortho*-dichlorobenzene, 65 °C for 24 h; then, *ortho*-dichlorobenzene, reflux for 7 h.

applied potential, and $V_{\rm bi}$ is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\rm bi} = 0$ V).

Figure 6 shows the *J*–*V* curves of the P3HT/F1–F5 blend films. The values of electron mobility were calculated from the plots of ln(*J*) versus ln(*V*). The electron mobilities obtained for the P3HT/F1–F5 blend films are 2.2×10^{-3} , 1.3×10^{-3} , 8.4×10^{-5} , 3.9×10^{-4} , and 2.8×10^{-4} cm² V⁻¹ s⁻¹, respectively. The electron mobility of 1.3×10^{-3} cm² V⁻¹ s⁻¹ for P3HT/F2(PCBM) is close to that reported in the literature (2.0×10^{-3} cm² V⁻¹ s⁻¹).^[26a] F1 shows a higher electron mobility than PCBM, and F3 displays the lowest electron mobility, which agrees with the higher *I*_{sc} value of the PSC with F1 as acceptor and the lower *I*_{sc} value of the PSC with F3 as acceptor.

2.5. Morphology

The morphology of the photoactive layer is very important for the photovoltaic performance of PSCs.^[5] We used atomic force microscopy (AFM) to investigate the morphology of the P3HT/F1-F5 (1:1, w/w) blend films. The AFM topography images are shown in Figure 7. We can see intuitively that there is obviously phase separation for all the blend films with bright islands for P3HT and dark valleys for the C₆₀ derivatives. There are large fullerene derivative aggregates being confined within the P3HT matrix, which implies that an interpenetrating network was formed in the blend films, which is beneficial for forming an efficient exciton dissociation interface and bicontinuous charge transport channels. The surface rms (root-mean-square) roughness of the P3HT/ F1-F5 films is 9.2, 15.8, 23.3, 14.2, and 13.6 nm respectively. The rough surface is a signature of P3HT self-organization, which enhances ordered structural formation in the thin film.^[5b] But too large a rms roughness of 23.3 nm for the P3HT/F3 film could be one reason for the lower photovoltaic performance.

3. Conclusions

A series of PCBM-like C_{60} derivatives with different alkyl chain lengths of their side chain, F1–F5, have been synthesized to investigate the effect of the alkyl chain length on the photovoltaic properties of the fullerene acceptors. The C_{60} derivatives show nearly the same absorption spectra and electrochemical properties, and their LUMO energy levels are almost the same as that of PCBM (F2) at approx. -3.9 eV, which indicates that the alkyl chain length influences the absorption and electronic energy levels of the C_{60} derivatives very little. The photovoltaic properties of the C_{60} derivatives were investigated by fabricating the PSC devices with P3HT as donor and F1-F5 as acceptor with the device structure of ITO/PEDOT:PSS/P3HT:F1-F5 (1:1, w/w)/Ca/Al. The PCEs of the PSCs based on P3HT/F1-F5 are 3.7%, 3.5%, 2.3%, 3.6%, and 2.8% respectively. Obviously, there is a significant and interesting influence of the alkyl chain length in the side chain of the PCBMlike molecules on the photovoltaic performance of the PSC devices based on P3HT/F1-F5, F1 with a one carbon shorter alkyl chain and F4 with a two carbons longer alkyl chain show similar or a little higher efficiency than PCBM, while F3 with a one carbon longer alkyl chain and F5 with a three carbons longer alkyl chain display lower efficiency than PCBM. The better photovoltaic performance of F1 may be a benefit of its strong absorption intensity, higher electron mobility, and optimum morphology of the P3HT/F1 blend film. While the poorer photovoltaic performance of F3 could suffer from its weaker absorption intensity, lower electron mobility, and poorer morphology of the P3HT/F3 film. The results indicate that the alkyl chain length on the side chain of the PCBM-like molecules significantly influence their absorption intensity, electron mobility, morphology of the films blended with P3HT, and the P3HT/ fullerene derivative interface structure, so that it influences the photovoltaic performance of the fullerene derivatives.

4. Experimental

Materials: 4-Phenylbutanoic acid, 5-phenylhexanoic acid, 6-phenylheptanoic acid, 7-phenyloctanoic acid, and 4-methylbenzenesulfonohydrazide were purchased from Alfa Co. C_{60} was obtained from Yongxin Co. (China). P3HT (4002E) was bought from Rieke Metals and used as received. PCBM (purity > 99.0%) was purchased from American Dye Inc. and used as received. Other reagents and solvents were obtained from the Beijing Chemical Co. as analytical grade quality and used as received.

Synthesis: The fullerene derivatives of F1–F5 were synthesized by the same method as that for the synthesis of PCBM.^[26] The synthetic route is shown in Scheme 2.

3-Phenylbutanoic Acid Methyl Ester, **2**: 4-Phenylbutanoic acid (0.1 mol) was added to 100 mL of methanol, and then 6 drops of sulfuric acid was added to the solution. The mixture was refluxed for 12 h and then cooled to room temperature. After evaporating the solvent, the crude product was





purified by silica gel chromatography eluted with a mixture of petroleum and ethyl acetate (5:1) to obtain **2**. ¹H NMR (300 MHz, CDCl₃, δ): 7.95 (d, 2H), 7.55 (m, 1H), 7.44 (t, 2H), 3.66 (s, 3H), 2.98 (t, 2H), 2.44 (t, 2H). EIMS (*m*/*z*): 192.

3-Phenylbutanoic Acid Methyl Ester Hydrazone, **3**: 4-Phenylbutanoic acid methyl ester (0.1 mol) and 4-methylbenzenesulfonohydrazide (0.11 mol) were added to 100 mL of methanol. The mixture was then refluxed for 12 h and cooled to room temperature. After evaporating the solvent, **3** was obtained by purification of the crude product by silica gel chromatography eluted with a mixture of petroleum and ethyl acetate (5:1). ¹H NMR (300 MHz, CDCl₃, δ): 9.75 (s, 1H), 7.95 (d, 2H), 7.78 (d, 1H), 7.55 (m, 2H), 7.44 (m, 2H), 7.30 (m, 1H), 7.17 (m, 1H), 3.64 (m, 3H), 2.95 (t, 2H), 2.61 (t, 2H), 2.44 (t, 3H). EIMS (*m*/*z*): 506.

5-Phenylhexanoic Acid Methyl Ester, 4: Compound 4 was prepared by the same method as the synthesis of compound 2, except 5-phenylhexanoic acid was used instead of 3-phenylbutanoic acid. ¹H NMR (300 MHz, CDCl₃, δ): 7.95 (d, 2H), 7.55 (m, 1H), 7.44 (t, 2H), 3.66 (s, 3H), 2.98 (t, 2H), 2.35 (t, 2H), 1.68 (m, 4H). EIMS (*m*/*z*): 220.

5-Phenylhexanoic Acid Methyl Ester Hydrazone, 5: Compound 5 was prepared by the same method as for the synthesis of compound 3, except compound 4 was used instead of compound 2. ¹H NMR (300 MHz, CDCl₃, δ): 8.35 (s, 1H), 7.96 (d, 2H), 7.63 (d, 2H), 7.55 (m, 2H), 7.44 (m, 1H), 7.30 (m, 1H), 7.17 (m, 1H), 3.67 (m, 3H), 2.61 (t, 2H), 2.44 (t, 5H), 1.45 (2H), 1.23 (t, 2H).

6-Phenylheptanoic Acid Methyl Ester, 6: Compound 6 was prepared by the same method as that for the synthesis of compound 2, except 6phenylheptanoic acid was used instead of 3-phenylbutanoic acid. ¹H NMR (300 MHz, CDCl₃, δ): 7.95 (d, 2H), 7.55 (m, 1H), 7.44 (t, 2H), 3.66 (s, 3H), 2.98 (t, 2H), 2.35 (t, 2H), 1.68 (m, 4H), 1.40 (t, 2H). EIMS (*m*/z): 235.

6-Phenylheptanoic Acid Methyl Ester Hydrazone, $\vec{7}$: Compound $\vec{7}$ was prepared by the same method as that for the synthesis of compound $\vec{3}$, except compound $\vec{6}$ was used instead of compound $\vec{2}$. ¹H NMR (300 MHz, CDCl₃, δ) \Box 8.01 (s, 1H), 7.90 (d, 2H), 7.77 (d, 2H), 7.63 (m, 2H), 7.45 (m, 1H), 7.33 (m, 1H), 7.03 (m, 1H), 3.67 (m, 3H), 2.61 (t, 2H), 2.44 (t, 5H), 1.45 (2H), 1.23 (t, 2H).

7-Phenyloctanoic Acid Methyl Ester, **8**: Compound **8** was prepared by the same method as that for the synthesis of compound **2**, except 7-phenyloctanoic acid was used instead of 3-phenylbutanoic acid. ¹H NMR (300 MHz, CDCl₃, δ): 7.95 (d, 2H), 7.56 (m, 1H), 7.43 (t, 2H), 3.66 (s, 3H), 2.98 (t, 2H), 2.33 (t, 2H), 1.68–1.62 (m, 6H), 1.37 (t, 2H). EIMS (*m*/*z*): 249.

7-Phenyloctanoic Acid Methyl Ester Hydrazone, **9**: Compound **9** was prepared by the same method as that for the synthesis of compound **2**, except compound **8** was used instead of compound **2**. ¹H NMR (300 MHz, $CDCl_3, \delta$): 8.01 (s, 1H), 7.920 (d, 2H), 7.77 (d, 2H), 7.65 (m, 2H), 7.43 (m, 1H), 7.31 (m, 1H), 7.03 (m, 1H), 3.67 (m, 3H), 2.61 (t, 2H), 2.44 (t, 5H), 1.45 (2H), 1.23 (t, 4H).

The C_{60} Derivatives: Under protection of nitrogen, compound **3** or **5** or **7** or **9** (4 mmol) was added to a 250 mL three-necked flask. Dry pyridine (30 mL) and NaOMe (225 mg) were then added. The mixture was stirred for 15 min at room temperature. A solution of 1.44 g of C_{60} in 100 mL of *ortho*-dichlorobenzene was then added to the above mixture. The mixture was heated to 65 °C and stirred for 24 h at this temperature. After evaporating the solvent, the crude product was dissolved in 100 mL of *ortho*-dichlorobenzene, and then was refluxed for 7 h. The solvents were then evaporated, the mixture was separated and purified by silica gel chromatography with toluene to get the C_{60} derivatives.

F1: ¹H NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 7.83 (d, 2H), 7.47 (t, 2H), 7.41 (t, 1H), 3.60 (s, 3H), 2.79 (t, 2H), 2.40 (t, 2H). ¹³C NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 172.02, 147.30, 145.77, 145.23, 145.11, 145.01, 144.82, 144.71, 144.54, 143.79, 143.10, 143.05, 143.00, 142.27, 142.18, 142.08, 141.11, 138.25, 136.11, 132.16, 128.70, 51.74, 50.85, 31.65, 30.14, 29.84. MALDI-TOF MS (*m*/*z*): 896.3. Anal. calcd for C₇₁H₁₂O₂: C 95.09, H 1.34, O 3.57; found: C 94.89, H 1.32, O 3.51.

F2: ¹H NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 7.83 (d, 2H), 7.47 (t, 2H), 7.41 (t, 1H), 3.57 (s, 3H), 2.83 (t, 2H), 2.32 (t, 2H), 2.02 (m, 2H). ¹³C NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 173.13, 148.85, 147.90, 146.02, 145.39, 145.25, 144.99, 144.87, 144.69, 144.28, 143.97, 143.21, 143.15, 142.33, 141.24, 138.26, 137.86, 136.86, 132.27, 128.71, 128.50, 52.02, 51.74, 34.10, 33.95, 30.18, 22.73. MALDI-TOF MS (*m/z*): 911.3. Anal. calcd for C₇₂H₁₄O₂: C 94.95, H 1.54, O 3.52; found: C 94.87, H 1.48, O 3.48.

F3: ¹H NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 7.83 (d, 2H), 7.47 (t, 2H), 7.41 (t, 1H), 3.57 (s, 3H), 2.83 (t, 2H), 2.32 (t, 2H), 1.80 (m, 4H). ¹³C NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 169.16, 144.90, 144.02, 142.00, 141.37, 141.26, 140.98, 140.87, 140.65, 140.27, 139.96, 139.15, 138.44, 138.32, 137.24, 136.97, 134.23, 133.82, 133.07, 128.36, 125.11, 124.94, 124.76, 48.34, 47.97, 30.28, 26.29, 22.93, 21.44. MALDI-TOF MS (*m*/*z*): 924.3. Anal. calcd for C₇₃H₁₆O₂: C 94.81, H 1.73, O 3.46; found: C 94.76, H 1.65, O 3.37.

F4: ¹H NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 7.88 (d, 2H), 7.47 (t, 2H), 7.41 (t, 1H), 3.57 (s, 3H), 2.82 (t, 2H), 2.26 (t. 2H), 1.84 (m, 2H), 1.66 (m, 2H), 1.46 (m, 2H). ¹³C NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 173.97, 150.53, 146.85, 146.37, 146.15, 145.78, 145.46, 144.65, 143.98, 143.82, 142.75, 142.48, 139.78, 134.62, 134.00, 132.83, 132.50, 132.16, 130.23, 129.91, 129.58, 81.80, 54.15, 53.56, 36.11, 35.86, 31.98, 31.43, 28.85, 27.11. MALDI-TOF: 938.4. Anal. calcd for C₇₄H₁₈O₂: C 94.67, H 1.92, O 3.41; found: C 94.56, H 1.87, O 3.36.

F5: ¹H NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 7.88 (d, 2H), 7.52 (t, 2H), 7.45 (t, 1H), 3.63 (s, 3H), 2.87 (t, 2H), 2.31 (t. 2H), 1.64 (m, 2H), 1.53 (m, 2H), 1.46–1.28 (m, 4H). ¹³C NMR (400 MHz, CS₂/CDCl₃ 3:1, δ): 173.88, 150.37, 146.66, 146.17, 145.96, 145.59, 145.27, 144.45, 143.78, 143.64, 142.56, 142.30, 139.18, 134.41, 133.80, 132.57, 132.24, 131.91, 129.94, 129.61, 129.29, 99.98, 81.67, 54.08, 53.26, 36.04, 35.69, 31.81, 31.47, 31.20, 28.81, 26.95. MALDI-TOF MS (*m*/*z*): 952.3. Anal. calcd for C₇₅H₂₀O₂: C 94.54, H 2.10, O 3.36; found: C 94.46, H 1.98, O 3.31.

Instrument and Measurements: ¹H NMR spectra were measured on a Bruker DMX-400 spectrometer, chemical shifts were reported in ppm relative to the singlet of CDCl₃ at 7.26 ppm, and splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. Photoluminescence spectra were conducted on a Hitachi F4500 spectrophotometer. Electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with a Pt disk, a Pt wire, and a Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) *ortho*-dichlorobenzene/acetonitrile solution mixture (5:1, v/v). The AFM measurement of the surface morphology of samples was conducted on a Nanoscope III (DI, USA) in contact mode with 5 μ m scanners.

Device Fabrication and Characterization: The PSCs were fabricated in the configuration of the traditional sandwich structure with an ITO glass positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of 10 Ω sq⁻¹ was purchased from CSG HOLDING Co., LTD (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min PEDOT: PSS (Clevious P VP AI 4083 H. C. Stark, Germany) was filtered through a 0.45 μ m filter and spin coated at 4000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT:PSS film was baked at 150 $^\circ\text{C}$ for 20 min in air. The thickness of the film was around 30 nm. The blend solution of P3HT and acceptors (F1-F5) in ortho-dichlorobenzene (DCB) (1:1, w/w, 36 mg mL^{-1}) was spin-coated on top of the PEDOT:PSS layer at 800 rpm for 30 s. The wet polymer/acceptor blend films were then put into glass Petri dishes to undergo the solvent annealing process [5b]. The thickness of the photoactive layer was in the range of 200-250 nm as measured using an Ambios Technology XP-2 profilometer. The negative electrode consisted of Ca (~20 nm) capped with Al (~100 nm) that was thermally evaporated under a shadow mask at a base pressure of $\sim 10^{-4}$ Pa. The device active area was ${\sim}4\text{--}6~\text{mm}^2$ for all the PSCs discussed in this work. The current-voltage (I-V) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in a glovebox under simulated AM1.5G irradiation (100 mW cm^{-2}) using a xenon-lamp-based solar simulator (from Newport Co., LTD). The EQE was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic







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cell. The measurement of electron mobilities was conducted in the dark by the space-charge limited current (SCLC) method on a computer-controlled Keithley 236 Source Measure Unit, for the electron-only devices. For the electron-only devices, Al film (60 nm) was thermally evaporated onto a glass slide. The P3HT:fullerene derivative solutions were spin-coated onto the Al film/glass substrate, and then the Al (100 nm) electrode was thermally evaporated onto the blend film through a shadow mask.

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