High-Yield Synthesis and Electrochemical and Photovoltaic Properties of Indene-C$_{70}$ Bisadduct

By Youjun He, Guangjin Zhao, Bo Peng, and Yongfang Li$^*$

[6, 6]-Phenyl-C$_{61}$-butyric acid methyl ester (PC$_{60}$BM) is the widely used acceptor material in polymer solar cells (PSCs). Nevertheless, the low LUMO energy level and weak absorption in visible region are its two weak points. For enhancing the solar light harvest, the soluble C$_{70}$ derivative PC$_{70}$BM has been used as acceptor instead of PC$_{60}$BM in high efficiency PSCs in recent years. But, the LUMO level of PC$_{60}$BM is the same as that of PC$_{70}$BM, which is too low for the PSCs based on the polymer donors with higher HOMO level, such as poly(3-hexylthiophene) (P3HT). Here, a new soluble C$_{70}$ derivative, indene-C$_{70}$ bisadduct (IC$_{70}$BA), is synthesized with high yield of 58% by a one-pot reaction of indene and C$_{70}$ at 180 °C for 72 h. The electrochemical properties and electronic energy levels of the fullerene derivatives and electronic energy levels of the fullerene are measured by cyclic voltammetry. The LUMO energy level of IC$_{70}$BA is 0.19 eV higher than that of PC$_{70}$BM. The PSC based on P3HT with IC$_{70}$BA as acceptor shows a higher $V_{oc}$ of 0.84 V and higher power conversion efficiency (PCE) of 5.64%, while the PSC based on P3HT/PC$_{60}$BM and P3HT/PC$_{70}$BM displays $V_{oc}$ of 0.59 V and 0.58 V, and PCE of 3.55% and 3.96%, respectively, under the illumination of AM1.5G, 100 mW cm$^{-2}$. The results indicate that IC$_{70}$BA is an excellent acceptor for the P3HT-based PSCs and could be a promising new acceptor instead of PC$_{70}$BM for the high performance PSCs based on narrow bandgap conjugated polymer donor.

1. Introduction

Since Gang Yu et al reported the bulk heterojunction polymer solar cells (PSCs) based on the conjugated polymer and fullerene in 1995,[1] PSCs have drawn broad attention from physical, material and chemical scientists,[2–12] owing to their advantages of easy fabrication, low cost, light weight and possibility to fabricate flexible devices. The photoactive layer of the PSCs is commonly composed of a blend film of a conjugated polymer donor and a soluble fullerene derivative acceptor.[1] The most representative polymer donor is poly(3-hexylthiophene) (P3HT), and the most important soluble fullerene derivative acceptor is [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{60}$BM). Power conversion efficiency (PCE) of the PSCs based on P3HT/PC$_{60}$BM have reached over 4% by device fabrication engineering.[13–16] Moreover, the high efficiency of the P3HT/PC$_{60}$BM devices is reproducible in different laboratories and insensitive to the active layer thickness of the devices in the range of 100 – 300 nm which is very important for future low cost and large area fabrication of the PSCs by solution-processing. However, further improvement of the photovoltaic performance of the PSCs based on P3HT/PC$_{60}$BM is limited by the mismatch of the P3HT absorption band with the solar spectrum, week visible absorption of PC$_{60}$BM and big energy loss during exciton charge separation at the interface of P3HT/PC$_{60}$BM.

Figure 1 shows the electronic energy levels of the active layer of the P3HT/PC$_{60}$BM based PSCs. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of P3HT are from the data reported by Hou et al.[13] and those of PC$_{60}$BM are measured in this work. The value of $\Delta E_{1}$, the difference between the LUMO levels of the donor and acceptor, provides the driving force for the charge separation of the excitons in the polymer donor to overcome the binding energy of the excitons. And the value of $\Delta E_{3}$, the difference between the LUMO level of the acceptor and the HOMO level of the donor, determines the open circuit voltage ($V_{oc}$).[14,15] Usually, the binding energy of the excitons is ca. 0.3 – 0.5 eV, for example, ca. 0.4 eV for PPV derivatives[16,17] and 0.45 eV for polythiophenes.[18] 0.5 eV of $\Delta E_{1}$ should be enough for the efficient charge separation. 1.17 eV of $\Delta E_{3}$ is too large, which results in a big energy loss in the exciton charge separation so that leads to a lower $V_{oc}$. Obviously, increasing the LUMO level of the fullerene acceptor will be beneficial to a higher $V_{oc}$ and higher photovoltaic efficiency of the devices.[19] Another weak point of PC$_{60}$BM is its weak absorption in visible region. Actually, [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{70}$BM) has been widely used instead of PC$_{60}$BM in the PSCs based on narrow bandgap polymer donors for enhancing the solar light harvest in the wavelength region of 350 – 500 nm.[7–12,20–23]
Various fullerene derivative acceptors have been reported for improving their solubility, increasing their electron mobility and tuning their LUMO energy level.12,24-34 But most of the new fullerene acceptors show poorer or similar photovoltaic performance in comparison with PC_{60}BM. Lenes et al. found that the LUMO level of PC_{60}BM bisadduct (bisPC_{60}BM) is ca. 0.1 eV higher than PC_{60}BM, and the PSC based on P3HT/bisPC_{60}BM showed a higher \( V_{oc} \) of 0.73 V and PCE of 4.5%.15,36 Ross et al. synthesized LuN@C_{60}-PCBH with LUMO energy level of -0.28 eV higher than PC_{60}BM, and the PSC based on P3HT/LuN@C_{60}-PCBH showed higher \( V_{oc} \) (0.26 V higher) than that of the device with PC_{60}BM as acceptor.24

Recently, we synthesized a new C_{60} derivative, indene-C_{60} bisadduct (IC_{60}BA) which possesses a LUMO level of 0.17 eV higher than that of PC_{60}BM. And the PSC based on P3HT/IC_{60}BA showed a higher \( V_{oc} \) of 0.84 V and a PCE of 5.64% under the illumination of AM1.5, 100 mW cm\(^{-2}\), while the PSC based on P3HT/PC_{60}BM and P3HT/PC_{70}BM displays \( V_{oc} \) of 0.59 V and 0.58 V, and PCE of 3.55% and 3.96% respectively, under the illumination of AM1.5G, 100 mW cm\(^{-2}\). Obviously, IC_{70}BA could be a promising new acceptor instead of PC_{70}BM for the high performance PSCs based on narrow bandgap conjugated polymer donor.

2. Results and Discussion

2.1. Synthesis of IC_{70}MA and IC_{70}BA

The synthetic route of IC_{70}BA (Scheme 1) is similar with the synthesis of IC_{60}BA38 with C_{70} instead of C_{60}. This is a simple one-pot reaction with starting chemicals of indene and C_{70} putting in o-dichlorobenzene solution refluxing at 180 °C for 12 – 72 h. The product is a mixture of indene-C_{70} monoadduct (IC_{70}MA), IC_{70}BA. Indene-C_{70} multiadduct and unreacted C_{70}. The pure IC_{70}BA and IC_{70}MA were separated and purified by silica gel column chromatography. The relative weight ratio of IC_{70}MA and IC_{70}BA in the product mixture is related to the reaction conditions including the molar ratio of indene to C_{70}, refluxing solvent, reaction temperature and time. The yield of IC_{70}BA could be easily improved by changing reaction conditions. For instance, by increasing the reaction time from 12 h to 72 h, and tuning the molar ratio of indene to C_{70} from 12 to 36, the yield of IC_{70}BA increased greatly from 8% to 58%, while the yield of IC_{70}MA decreased from 18% to 6.3%. The high yield synthesis is very important for future application of IC_{70}BA.

The molecular structure of IC_{70}MA and IC_{70}BA was confirmed by \(^1\)H-NMR and \(^{13}\)C-NMR spectra, MALDI-TOF mass spectra and elemental analysis. The MALDI-TOF mass spectra, \(^1\)H-NMR and \(^{13}\)C-NMR spectra of IC_{70}MA and IC_{70}BA are shown in Figure S1 – S6 in the Supporting Information. According to the elemental analysis, the purity of the IC_{70}BA product is 98.6%. IC_{70}BA possesses good solubility in common organic solvents such as THF, chloroform, toluene, o-dichlorobenzene. But the solubility of IC_{70}MA is poorer.
It should be mentioned that IC$_{70}$BA product could be a mixture of different isomers as that of IC$_{60}$BA which is a mixture of six isomers[39] Prof. D. I. Schuster’s group have done a lot of work on the structural characterization of the fullerene bisadducts isomers.[40–42] In this work, we mainly concern the LUMO energy level of IC$_{70}$BA bisadducts and its photovoltaic properties, and the isomers of the bisadduct have little effect on the LUMO energy level and photovoltaic properties,[35–36,38] so we didn’t distinguish the isomers of IC$_{70}$BA.

2.2. Absorption Spectra of IC$_{70}$MA and IC$_{70}$BA

The absorption property, especially the absorption in visible region, is very important for the photovoltaic materials. Figure 2 shows the UV-Vis absorption spectra of IC$_{70}$MA, IC$_{70}$BA, PC$_{60}$BM and PC$_{70}$BM in dilute THF solutions with a concentration of 10$^{-3}$ mol L$^{-1}$. In the UV-visible region from 200 to 700 nm, the absorbance of the C$_{60}$ derivatives, including PC$_{60}$BM, IC$_{70}$MA and PC$_{70}$BM, is similar and much stronger than that of PC$_{60}$BM. In the visible region from 400 nm to 700 nm, the three C$_{60}$ derivatives show quite strong absorption, in comparison with the very weak absorption of PC$_{60}$BM in the visible region (see the inset of Figure 2). Comparing the visible absorption of the three C$_{70}$ derivatives, IC$_{70}$MA is a little stronger while IC$_{70}$BA is a little weaker than PC$_{70}$BM. The stronger visible absorption is an advantage of the C$_{70}$ derivatives over C$_{60}$ derivatives for them to be used as acceptor in polymer solar cells.

2.3. Electrochemical Properties of IC$_{70}$MA and IC$_{70}$BA

The electrochemical properties of IC$_{70}$MA, IC$_{70}$BA, PC$_{60}$BM and PC$_{70}$BM were studied by cyclic voltammetry. Figure 3 shows the cyclic voltammograms of the fullerene derivatives in the potential range of 2.0 ~ −2.5 V vs. Ag/Ag$^+$. In the negative potential range, it can be seen that the fullerene derivatives exhibit three well-defined, reversible reduction waves respectively in the potential range from −0.7 V to −2.2 V. Table 1 listed the half-wave potentials (defined as $E = 0.5(E_{p,a} + E_{p,c})$ where $E_{p,a}$ is the cathodic peak potential and $E_{p,c}$ is the corresponding anodic peak potential) of the reduction processes of the three C$_{70}$ derivatives together with that of PC$_{60}$BM for comparison. The electrochemical reduction property of PC$_{70}$BM is similar with that of PC$_{60}$BM. Comparing the three C$_{70}$ derivatives, the first ($E_1$), second ($E_2$) and third ($E_3$) reduction potentials all shifted negatively from PC$_{60}$BM to IC$_{70}$MA to IC$_{70}$BA. $E_1$ is shifted from −0.88 V for PC$_{60}$BM to −0.93 V (shifted by −0.05 V) for IC$_{70}$MA and to −1.07 V (shifted by −0.19 V) for IC$_{70}$BA. $E_2$ is shifted from −1.28 V for PC$_{70}$BM to −1.31 V (shifted by −0.03 V) for IC$_{70}$MA and to −1.43 V (shifted by −0.15 V) for IC$_{70}$BA. $E_3$ is shifted from −1.70 V for PC$_{70}$BM to −1.71 V (shifted by −0.01 V) for IC$_{70}$MA and to −1.92 V (shifted by −0.22 V) for IC$_{70}$BA. Obviously, the indene addition on C$_{70}$ results in negative shift of the reduction potentials, and the second addition of indene on C$_{70}$ in IC$_{70}$BA induce

**Table 1.** The half-wave potentials of the reduction processes, onset reduction and oxidation potentials, LUMO and HOMO energy levels of the fullerene derivatives

<table>
<thead>
<tr>
<th>fullerene derivatives</th>
<th>$E_1$ [V]</th>
<th>$E_2$ [V]</th>
<th>$E_3$ [V]</th>
<th>$E_{onset}^{red}$ [V]</th>
<th>$E_{onset}^{ox}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{60}$BM</td>
<td>−0.88</td>
<td>−1.28</td>
<td>−1.78</td>
<td>1.22/−5.93</td>
<td>−0.80/−3.91</td>
</tr>
<tr>
<td>PC$_{70}$BM</td>
<td>−0.88</td>
<td>−1.28</td>
<td>−1.70</td>
<td>1.16/−5.87</td>
<td>−0.80/−3.91</td>
</tr>
<tr>
<td>IC$_{70}$MA</td>
<td>−0.93</td>
<td>−1.31</td>
<td>−1.71</td>
<td>1.08/−5.79</td>
<td>−0.86/−3.85</td>
</tr>
<tr>
<td>IC$_{70}$BA</td>
<td>−1.07</td>
<td>−1.43</td>
<td>−1.92</td>
<td>0.90/−5.61</td>
<td>−0.99/−3.72</td>
</tr>
</tbody>
</table>

[a] The potential values in this table are versus Ag/Ag$^+$ reference electrode.
much stronger negative shift of the reduction potential of the C70 derivatives.

The LUMO energy levels of the fullerene derivatives were estimated from their onset reduction potentials indicated in the cyclic voltammograms.[43] The onset reduction potentials ($E_{\text{on}}^{\text{red}}$) of PC70BM, IC70MA and IC70BA were $-0.80$, $-0.85$ and $-0.99$ V vs. Ag/Ag⁺, respectively. From the onset reduction potentials, the LUMO energy levels of the molecules were calculated according to the equation:[44] $\text{LUMO} = -e (E_{\text{on}}^{\text{red}} + 4.71)$ where $E_{\text{on}}^{\text{red}}$ is the onset reduction potential with the unit of V vs. Ag/Ag⁺. The LUMO energy levels of PC70BM, IC70MA and IC70BA calculated in this way are $-3.91$ eV, $-3.86$ eV and $-3.72$ eV respectively. The LUMO energy levels and the onset reduction potentials of the fullerene derivatives were also listed in Table 1. The LUMO level of IC70BA is raised by $0.19$ eV in comparison with that of PC70BM. The higher LUMO energy level of IC70BA is desirable for its application as acceptor in PSCs to get higher open-circuit voltage.

Figure 3 also shows the cyclic voltammograms of oxidation of the fullerene derivatives in the positive potential range of 0 to 2.0 V vs. Ag/Ag⁺. Interestingly, the C70 derivatives display two irreversible oxidation peaks in the potential range from 0.8 V to 2.0 V. The first oxidation peak shifted to lower potential from PC70BM at ca. 1.34 V to IC70MA at ca. 1.27 V (shifted by $-0.07$ V) to IC70BA at 1.06 V (shifted by $-0.28$ V), while the second oxidation peak remains in the same potential range for the three C70 derivatives. The HOMO energy levels of the fullerene derivatives were calculated according to the cyclic voltammograms of Figure 3. The onset oxidation potentials ($E_{\text{on}}^{\text{ox}}$) of PC70BM, PC70BM, IC70MA and IC70BA are 1.22, 1.16, 1.08 and 0.90 V vs. Ag/Ag⁺, respectively. From the onset oxidation potentials, the HOMO energy levels of the molecules were calculated according to the equation:[44] $\text{HOMO} = -e (E_{\text{on}}^{\text{ox}} + 4.71)$ where $E_{\text{on}}^{\text{ox}}$ is the onset oxidation potential with the unit of V vs. Ag/Ag⁺. The HOMO energy levels of PC70BM, PC70BM, IC70MA and IC70BA calculated in this way are $-5.93$, $-5.87$, $-5.79$ and $-5.61$ eV respectively. The onset oxidation potentials and the HOMO energy levels are also listed in Table 1. It should be noticed that the HOMO energy level of PC70BM at $-5.93$ eV measured by the electrochemical method is quite close to the value of $-6.0$ eV estimated from its ionization potential measured by photo-electron spectroscopy.[45]

The results indicate that the HOMO energy levels of IC70MA and IC70BA also moved upwards in comparison with that of PC70BM.

### 2.3. Photovoltaic Properties of IC70BA

For investigating the photovoltaic properties of IC70BA, PSCs were fabricated with P3HT as donor and IC70BA as acceptor, and the weight ratio of the donor to acceptor was 1:1. For comparison, the PSC devices based on P3HT/PC70BM and P3HT/PC70BM were also fabricated with commercial PC70BM and PC70BM as acceptor. Because of the poorer solubility of IC70MA in o-dichlorobenzene, we didn’t report the photovoltaic property of IC70MA.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** a) $J–V$ curves and b) EQE of the PSCs based on P3HT as donor and fullerene derivatives as acceptors with weight ratio of 1:1.

Table 2 shows the current density–voltage ($J–V$) curves of the three PSC devices with P3HT as donor and PC70BM, PC70BM or IC70BA as acceptor processed with solvent annealing[21] (for P3HT/IC70BA system, the film was annealed at 150 °C for 10 min after solvent annealing), under the illumination of AM1.5G, 100 mW cm⁻². The results of open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF) and power conversion efficiency (PCE) of the devices are listed in Table 2. It can be seen that $V_{oc}$ is increased from 0.59 V for the PC70BM-based PSC and 0.58 V for the PC70BM-based PSC to 0.84 V for the IC70BA-based PSC. The $V_{oc}$ of IC70BA-based device increases by ca. 40% in comparison with the PC70BM-based device. Obviously, the $V_{oc}$ increment of the IC70BA-based device.

### Table 2. Photovoltaic performance of the P3HT-based PSCs with different acceptors, under the illumination of AM1.5G, 100 mW cm⁻².

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm⁻²]</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC70BM</td>
<td>0.59</td>
<td>9.26</td>
<td>0.65</td>
<td>3.55%</td>
</tr>
<tr>
<td>PC70BM</td>
<td>0.58</td>
<td>10.04</td>
<td>0.68</td>
<td>3.96%</td>
</tr>
<tr>
<td>IC70BA</td>
<td>0.84</td>
<td>9.73</td>
<td>0.69</td>
<td>5.64%</td>
</tr>
<tr>
<td>IC70BA [a]</td>
<td>0.83</td>
<td>11.34</td>
<td>0.63</td>
<td>5.79%</td>
</tr>
</tbody>
</table>

[a] The best device performance of the P3HT/IC70BA PSC.
PSC is benefited from the higher LUMO energy level of IC70BA, because it is well known that $V_{oc}$ of the PSCs is proportional to the difference between the HOMO of the donor (here it is P3HT) and the LUMO of the acceptor.\[14\] The $J_{sc}$ is decreased from 10.04 mA cm$^{-2}$ for PC60BM-based device to 9.73 mA cm$^{-2}$ for IC70BA-based device. The significant increase in $V_{oc}$ leads to a higher PCE of 5.64% for the IC70BA-based PSC, which is ca. 43% increased in comparison with the PCE of 3.96% for the PC70BM-based device and 59% increased in comparison with the PCE of 3.55% for the PC60BM-based devices. In fact, the best PCE of the P3HT/IC70BA device we obtained reached 5.79% with a $V_{oc}$ of 0.81 V, a $J_{sc}$ of 11.34 mA cm$^{-2}$ and a FF of 0.63.

It should be mentioned that thermal annealing is very important for the PSCs based on P3HT/IC70BA. Before the thermal annealing, the $V_{oc}$, $J_{sc}$ and FF of the devices with IC70BA as acceptor were 0.85 V, 5.19 mA cm$^{-2}$ and 0.47. The lower $J_{sc}$ and FF resulted in lower PCE of 2.05%. After thermal annealing at 150 °C for 10 min, the $J_{sc}$ and FF of the device were greatly increased to 9.73 mA cm$^{-2}$ and 0.69 respectively, and PCE was increased to 5.64%. External quantum efficiency (EQE) of the device based on P3HT/PC60BM and P3HT/IC70BA after annealing at 150 °C for 10 min is shown in Figure 4b. High EQE values were observed in the wavelength range of 380 – 650 nm for the two devices and the EQE value of the IC70BA-based PSC is higher than that of the PC60BM-based PSC (which is consistent with the higher $J_{sc}$ of the IC70BA-based device). The bigger increase of the EQE of the IC70BA-based PSC than PC60BM-based PSC in the wavelength of 380 – 500 nm and 650 – 700 nm could be ascribed to the contribution of the absorption of the C70 derivative acceptor. The EQE result indicates that the IC70BA acceptor is beneficial to the solar light harvest and photo-current conversion of the P3HT-based PSCs.

In order to understand the effect of the thermal annealing on the photovoltaic performance of the P3HT/IC70BA based PSC, we measured the absorption spectra of the P3HT/IC70BA blend films before and after the thermal annealing, together with the absorption spectra of the blend films of P3HT/PC60BM and P3HT/PC70BA for comparison, as shown in Figure 5. The blend films were prepared by the same method as that in the photovoltaic device fabrication. Before thermal annealing, the absorbance of P3HT/PC70BM film is the highest among the three blend films in the wavelength range of 350 – 650 nm. The peak intensity of P3HT/IC70BA film is between that of P3HT/PC60BM and P3HT/PC70BM films. After thermal annealing, the absorbance of the P3HT/IC70BA film in the wavelength of 350 – 550 nm increased significantly, while that of the P3HT/PC70BM films changed little. Obviously, the thermal annealing could improve the aggregation and absorption of the fullerene derivative IC70BA.

Figure 6 shows the AFM images of the P3HT/IC70BA film before and after the thermal annealing at 150 °C for 10 min. Before thermal annealing, the surface of the blend film is mainly occupied by P3HT nanofibers, little IC70BA appears on the surface. After thermal annealing, almost half surface is occupied by IC70BA and the interpenetrating donor-acceptor networks were formed. Obviously, the morphology change of the P3HT/IC70BA film after thermal annealing is beneficial to the improvement of the photovoltaic performance of the P3HT/IC70BA based PSCs.

3. Conclusions

In conclusion, we synthesized a new C70 derivative, indene-C70 bisadduct (IC70BA) with high yield of 58% by a one-pot reaction of indene and C70. IC70BA is highly soluble in common organic solvents and possesses 0.19 eV higher LUMO energy level than PC70BM. The PSCs based on P3HT/IC70BA show higher PCE of 5.64% with a higher $V_{oc}$ of 0.84 V (the best device displayed a highest PCE of 5.79% with a $V_{oc}$ of 0.81 V, a $J_{sc}$ of 11.34 mA cm$^{-2}$ and a FF of 0.63), under the illumination of AM1.5, 100 mW cm$^{-2}$, which is significantly improved in comparison with the $V_{oc}$ of 0.59 V and PCE of 3.55% of the device with PC60BM as acceptor and $V_{oc}$ of 0.58 V and PCE of 3.96% of the device with PC70BM as acceptor. IC70BA is an excellent acceptor for the P3HT-based PSCs and could be a promising new acceptor instead of PC70BM for further improving the PCE of the high performance PSCs based on narrow bandgap conjugated polymer donor by increasing open circuit voltage.
4. Experimental Section

Materials: Indene (99%) was purchased from Sigma-Aldrich Company. o-Dichlorobenzene was obtained from Alfa-Aesar Company. P3HT was purchased from Rieke Metals and used as received. PC_{60}BM and PC_{70}BM were bought from American Dyefunds Company and used as received. Other materials are commercially available.

Measurements: 1H-NMR and 13C-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 77 ppm for 1H-NMR and 13C-NMR respectively. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt wire, and Ag/Ag⁺ electrode (0.01 mol L⁻¹ AgNO₃, 0.09 mol L⁻¹ Bu₄NPF₆ in acetonitrile) as working electrode, counter electrode, and reference electrode respectively, in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) o-dichlorobenzene/acetonitrile (5:1) solution.

Synthesis of indene-C_{70} Bisadduct: The synthetic route of IC_{70}BA is shown in Scheme 1. Indene (2.78 g, 24 mmol) and C_{70} (1.68 g, 2 mmol) were dissolved in 60 mL o-dichlorobenzene, the solution was heated to 180 °C and then refluxed for 12 h. Then the reaction mixture was cooled to room temperature and added into 400 mL methanol. The residue was washed by methanol for several times. After removing the solvents, the residue was dissolved in 200 mL toluene and re-absorbed on silica gel, and was purified by silica gel column chromatography with 10% toluene in hexane. After removing unreacted C_{70}, 344 mg IC_{70}MA (yield: 18%) and 175 mg IC_{70}BA (yield: 8%) were obtained. When increasing the reaction time to 72 h, and increasing the amount of indene to 8.35 g (0.072 mol), 120 mg IC_{70}MA (yield: 6.3%) and 1.245 g IC_{70}BA (yield: 58%) were achieved.

Structural Analysis of IC_{70}BA: 1H NMR (300 MHz, CDCl₃, δ): 7.80–7.00 (m, 8H), 5.40–4.30 (m, 2H), 4.10–3.20 (m, 2H), 3.10–2.50 (m, 2H). 13C-NMR (300 MHz, CDCl₃, δ): 155.53, 151.93, 151.46, 151.28, 150.90, 150.71, 150.44, 149.17, 148.77, 148.53, 147.79, 147.41, 142.98, 141.54, 133.31, 128.36, 126.33, 125.17, 123.05, 69.11, 68.30, 67.52, 58.87, 57.50, 55.88, 46.44, 31.54, 29.89, 28.30, 22.40, 20.90. Elemental analysis for C₈₈H₁₆. Calculated: C, 98.51%; H, 1.49%. Found: C, 97.13%; H, 2.02%. MALDI-TOF MS: calcd for C₈₈H₁₆ 1073; found 1073.5. The purity of IC_{70}BA is about 98.6% from the result of elemental analysis.

Fabrication and Characterization of PSCs: The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (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 isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. Then PEDOT:PSS (poly (3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron P VPAI 4083, Germany) was filtered through a 0.45 μm filter and spin coated at 4000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT: PSS film was baked at 150 °C for 20 min in the air. The thickness of the film was around 30 nm. The blend solution of P3HT and different fullerene derivative acceptors in dichlorobenzene (DCB) (20 mg mL⁻¹ for each chemical except for P3HT/IC_{70}BA in which 17 mg mL⁻¹ is for each chemical) was then spin-coated on top of the PEDOT:PSS layer. The blend films were then put into glass petridishes while still wet to undergo solvent annealing process.[2] The thickness of...
of the photoactive layer is in the range of 180–220 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisted of 

Device characterization was done in glovebox under simulated AM1.5G irradiation (100 mW cm$^{-2}$). The J–V measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in glovebox under simulated AM1.5G irradiation (100 mW cm$^{-2}$) using a xenon-lamp-based solar simulator (from Newport Co., LTD). The EQE measurements of the PSCs were performed by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. P3HT:fullerene derivatives blend films for UV-vis absorption measurements were prepared on a quartz substrate. The absorption spectra were obtained using a Perkin–Elmer Lambda 12 UV-vis spectrophotometer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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