Indene−C₆₀ Bisadduct: A New Acceptor for High-Performance Polymer Solar Cells

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Abstract: Polymer solar cells (PSCs) are commonly composed of a blend film of a conjugated polymer donor and a soluble C_{60} derivative acceptor sandwiched between an ITO anode and a low-workfunction metal cathode. Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) are the most widely used donor and acceptor materials, respectively. However, the low LUMO energy level of PCBM limits the open circuit voltage (V_{oc}) of the P3HT-based PSCs to ca. 0.6 V. Here we synthesized a new soluble C_{60} derivative, indene−C_{60} bisadduct (ICBA), with a LUMO energy level 0.17 eV higher than that of PCBM. The PSC based on P3HT with ICBA as acceptor shows a higher V_{oc} of 0.84 V and higher power conversion efficiency (PCE) of 5.44% under the illumination of AM1.5, 100 mW/cm², while the PSC based on P3HT/PCBM displays a V_{oc} of 0.58 V and PCE of 3.88% under the same experimental conditions. The results indicate that ICBA is an alternative high-performance acceptor and could be widely used in high-performance PSCs.

Introduction

Polymer solar cells (PSCs) have drawn broad attention in recent years,[1−12] owing to their advantages of easy fabrication, low cost, light weight, and possibility to fabricate flexible devices.[13−15] The photoactive layer of the PSCs is commonly composed of a bulk-heterojunction-structured blend film of conjugated polymer donor and soluble fullerene derivative acceptor.[1] Broad visible−NIR absorption, higher charge carrier mobility, and suitable electronic energy levels of both the donor and acceptor materials are crucial for high-efficiency PSCs.[16] Poly(3-hexylthiophene) (P3HT) is the most representative conjugated polymer donor material, and [6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) is the most important acceptor material. A power conversion efficiency (PCE) of 4−5% has been reached for the PSCs based on the P3HT/PCBM system by device optimization.[3−5] In order to further improve the PCE of the PSCs, much research work has been devoted to finding new conjugated polymer donor materials aiming at broader absorption, lower bandgap, higher hole mobility, and suitable electronic energy levels, and some D−A copolymers show higher photovoltaic efficiency than P3HT.[6−10,17−23] Nevertheless, the research efforts toward new C_{60} derivative acceptor materials to replace PCBM have not been very successful until now.

For the acceptor materials in the PSCs, PCBM offers the advantages of good solubility in organic solvents (chloroform, chlorobenzene, dichlorobenzene, etc.), higher electron mobility,

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Scheme 1. Synthetic Route to ICBA
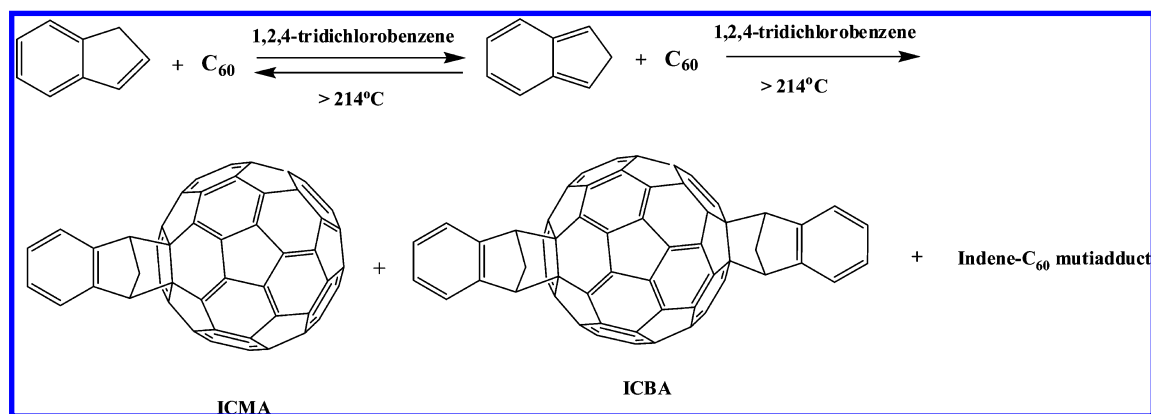
and higher electron affinity.[1−6] However, weak absorption in the visible region and a low LUMO energy level are its weak points. Weak absorption in the visible region limits its contribution to light harvesting in the photovoltaic conversion. The low LUMO energy level of the acceptor material results in lower open circuit voltage (V_{oc}) of the PSCs, since the V_{oc} of the PSCs is proportional to the difference between the LUMO energy level of the acceptor and the HOMO energy level of the donor.[24] Therefore, it is very important to design and synthesize new soluble fullerene derivatives with stronger visible absorption and higher LUMO energy levels than PCBM. Although many C_{60} derivatives[25−32] and a new C_{84} derivative[33] have been synthesized and used as acceptors in PSCs, most of the device performance is poorer than or similar to that of PCBM. It is worth notice that [6,6]-phenyl-C-71-butyric acid methyl ester (PC70BM) shows improved photovoltaic performance over PCBM in some cases,[20−23,34] a benefit of its stronger visible absorption. PCBM bisadduct (bisPCBM) shows ca. 0.1 eV higher LUMO energy level than PCBM, and the PCE of the PSC based on P3HT and bisPCBM reached 4.5%, an increase

of 18% over that of PCBM, which results from a higher V_{oc} of 0.73 V owing to the higher LUMO energy level of the acceptor.[35] Recently, Ross et al. reported a novel endohedral fullerene, $Lu_3N@C_{80}$-PCBH, which also possesses a higher LUMO energy level than PCBM.[36] The P3HT-based PSCs with $Lu_3N@C_{80}$-PCBH as acceptor showed higher V_{oc} (0.26 V higher) than the device with PCBM as acceptor. However, the high cost of $PC_{70}BM$ and $Lu_3N@C_{80}$-PCBH will limit their future commercial application in PSCs.

Here, we report a new C_{60} derivative, indene−C_{60} bisadduct (ICBA), shown in Scheme 1. ICBA is easily synthesized from C_{60} and indene−easier than the synthesis of PCBM. It possesses better solubility in common organic solvents (>90 mg/mL in chloroform) than PCBM and stronger visible absorption than PCBM. The LUMO energy level of ICBA is 0.17 eV higher than that of PCBM. The PSC based on P3HT with ICBA as acceptor demonstrated a higher V_{oc} of 0.84 V and a PCE of 5.44% under the illumination of AM1.5, 100 mW/cm^2, while the PSC based on the P3HT/PCBM system displays a V_{oc} of only 0.58 V and PCE of 3.88% under the same experimental conditions. Obviously, ICBA is superior to PCBM when it is used as acceptor in the P3HT-based PSCs.

Experimental Section

Materials. Indene (99%) was purchased from Sigma-Aldrich Co. C_{60} was purchased from Yongxin Co. (China). o-Dichlorobenzene and 1,2,4-trichlorobenzene were purchased from Alfa-Aesar Co. P3HT was purchased from Rieke Metals and used as received. PCBM was purchased from Nano-C and used as received. Other materials were commercially available.

Measurements. ^1H and ^{13}C NMR spectra were measured on a Bruker DMX-400 spectrometer. Chemical shifts were reported in ppm relative to the singlet of CDCl$_3$ at 7.26 and 77 ppm for ^1H and ^{13}C NMR, respectively. Absorption spectra were taken on a Hitachi U-3010 UV−vis spectrophotometer. Electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with Pt disk, Pt wire, and Ag/Ag$^+$ electrode (0.01 M AgNO$_3$, 0.09 M Bu$_4$NPF$_6$ in acetonitrile) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) o-dichlorobenzene/acetonitrile (5:1) solution.

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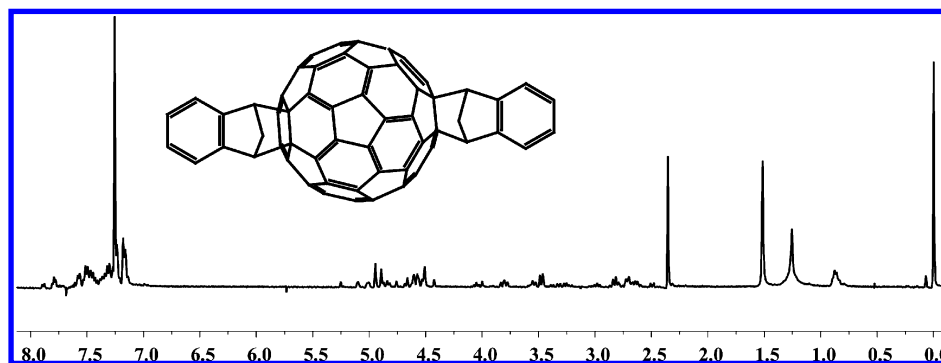
Figure 1. ^{1}H NMR spectrum of ICBA.

Synthesis of Indene—C$_{60}$ Bisadduct. The synthetic route to ICBA is shown in Scheme 1. Indene (4.63 g, 40 mmol) and C$_{60}$ (1.44 g, 2 mmol) were dissolved in 60 mL of 1,2,4-trichlorobenzene, and then the solution was heated to 220 °C and refluxed for 12 h. Subsequently, the reaction mixture was added into 400 mL of methanol and washed with methanol several times. After the solvents were removed, the residue was dissolved in 200 mL of toluene and re-absorbed on silica gel. The unreacted C$_{60}$, indene—C$_{60}$ monoadduct (ICMA), and ICBA were separated and purified by silica gel column chromatography with 10% toluene in hexane several times. A total of 428 mg of ICMA (yield 25%) and 653 mg of ICBA (yield 34%) were obtained.

When o-dichlorobenzene was used as solvent, indene (2.78 g, 24 mmol) and C$_{60}$ (1.44 g, 2 mmol) in 200 mL of o-dichlorobenzene were refluxed at 180 °C for 12 h, and 487 mg of ICBA was achieved (yield 26%).

^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 7.8—7.0 (m, 8H), 2.35 (s, 2H), 1.52 (s, 2H), 1.25 (s, 2H), 0.93 (s, 2H). ^{13}C NMR (CDCl$_3$, 300 MHz): δ (ppm) 160.86, 157.35, 155.76, 155.03, 153.88, 153.34, 149.24, 148.91, 148.34, 147.97, 147.81, 147.26, 146.40, 146.12, 145.79, 145.41, 145.17, 144.81, 143.78, 143.07, 142.60, 142.31, 141.43, 139.51, 138.02, 136.96, 129.20, 128.38, 127.28, 125.46, 124.12, 123.72, 74.77, 58.18, 57.34, 46.20, 29.87, 21.61. Elemental analysis for C$_{78}$H$_{16}$: calcd C 98.32, H 1.68%; found C 95.54, H 2.60. MALDI-TOF MS: calcd for C$_{78}$H$_{16}$ 953.0; found 953.4. The purity of the ICBA product is about 97%.

Fabrication and Characterization of PSCs. P3HT and different acceptors (1:1 wt ratio, 20 mg/mL for each) were dissolved in dichlorobenzene (DCB) separately to make a blend solution. The solution was then spin-coated on indium tin oxide (ITO)/glass substrates with a precoated poly(ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) layer. The polymer/acceptor blend films were then put into glass Petri dishes while still wet to undergo the solvent annealing process (see ref 3). The thickness of the photoactive layer is in the range of 180—220 nm. A bilayer cathode consisting of a calcium layer (20 nm) and subsequently an aluminum layer (100 nm) was deposited by thermal evaporation under vacuum (1 × 10^{-6} Torr). The device active area is ~0.1 cm^2 for all the solar cell devices discussed in this work. Device characterization was done in air after encapsulation under simulated AM1.5G irradiation (100 mW cm^{-2}) using a xenon-lamp-based solar simulator. The external quantum efficiency (EQE) measurements of the encapsulated devices were performed in air (PV Measurements Inc., model QEX7). Some oxidization of the electrodes (Ca/Al) was observed when devices were moved to air.

Results and Discussion

Synthesis of ICMA and ICBA. The synthetic route to indene—C$_{60}$ bisadduct (ICBA) is shown in Scheme 1. It is similar with the synthesis of indene—C$_{60}$ monoadduct (ICMA)

reported by Puplovskis et al.,[37] but we used 1,2,4-trichlorobenzene as the reaction solvent instead of o-dichlorobenzene in order to increase the yield of ICBA product. This is a simple one-pot reaction in which the starting chemicals, indene and C$_{60}$, are put in 1,2,4-trichlorobenzene solution and refluxed at 220 °C for 12 h. The product is a mixture of ICMA, ICBA, indene—C$_{60}$ mutiadduct, and unreacted C$_{60}$. The ICBA and ICMA were separated and purified by silica gel column chromatography. The synthesis of ICBA is easier than that of PCBM. The relative weight ratio of ICMA, ICBA, and indene—C$_{60}$ mutiadduct in the product mixture is related to the reaction conditions, including the molar ratio of indene to C$_{60}$, fluxing solvent, reaction temperature, and time. For instance, when using 1,2,4-trichlorobenzene as solvent and a molar ratio of indene to C$_{60}$ equal to 20, the yield of ICBA was 34%, whereas when using o-dichlorobenzene as solvent and a molar ratio of indene to C$_{60}$ equal to 12, the yield of ICBA decreased to 26%.

The structure of ICBA was confirmed by ^{1}H and ^{13}C NMR spectra, MALDI-TOF mass spectrum, and elemental analysis. The ^{1}H and ^{13}C NMR spectra of ICBA are shown in Figures 1 and 2, respectively. According to the elemental analysis, the purity of the ICBA product is 97%.

ICBA possesses excellent solubility in common organic solvents such as THF, chloroform, toluene, and o-dichlorobenzene (ICBA > 90 mg/mL in chloroform; PCBM > 80 mg/mL in chloroform).

Optical Properties of ICMA and ICBA. Absorption, especially in the visible region, is a very important property for the photovoltaic materials. PC$_{70}$BM is superior to PCBM (or PC$_{60}$BM) in many cases when it is used as the acceptor material in PSCs,[20−23,34] mainly benefiting from the stronger visible absorption of PC$_{70}$BM. Figure 3 shows the UV−vis absorption spectra of ICMA, ICBA, and PCBM in dilute THF solutions with a concentration of 10^{-5} mol/L. In the UV region from 200 to 300 nm, the absorption peaks of ICBA and ICMA are obviously weaker than that of PCBM. Interestingly, in the visible region from 400 to 800 nm, the absorbance of ICBA is much stronger than those of PCBM and ICMA, as shown in the inset of Figure 3. In the visible absorption spectrum of ICMA, there is a sharp peak at ca. 430 nm and a weak peak at ca. 700 nm, which is consistent with the literature.[37] The absorbance of ICMA between 400 and 500 nm is stronger than that of PCBM. The visible absorbance of ICBA is further enhanced from that of ICMA and shows a red-shifted weak peak at ca. 720 nm.

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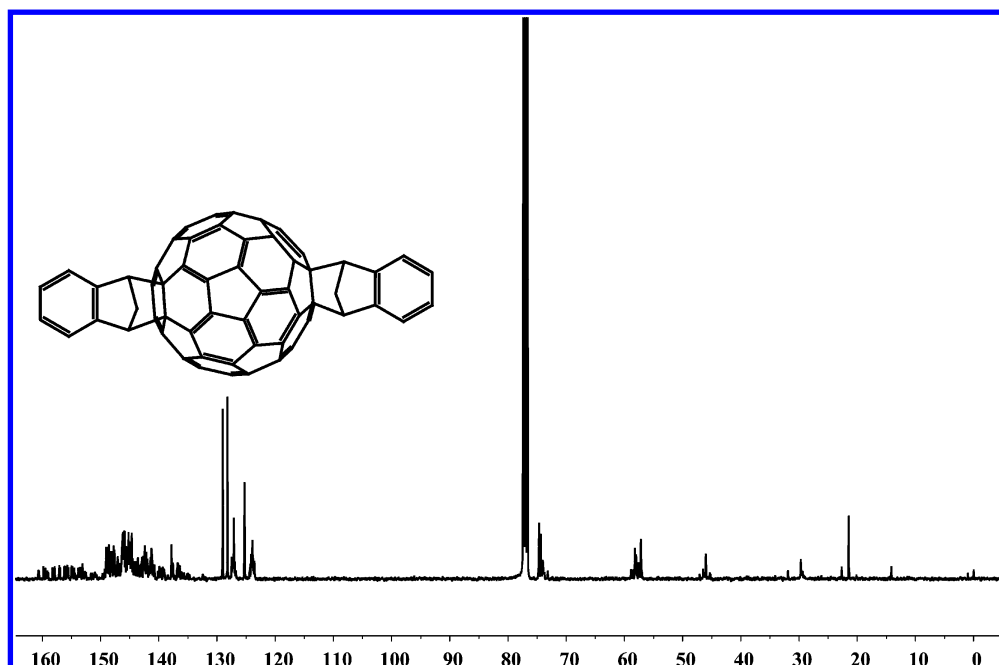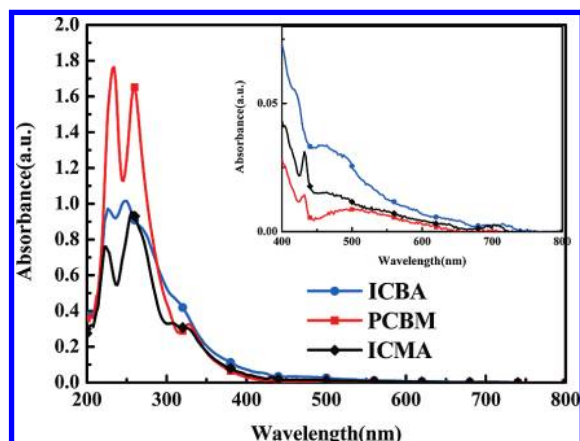
Figure 2. ^{13}C NMR spectrum of ICBA.

Figure 3. Absorption spectra of ICMA, ICBA, and PCBM in THF solutions (10^{-5} mol/L). Inset: Enlarged absorption spectra in the visible region from 400 to 800 nm.
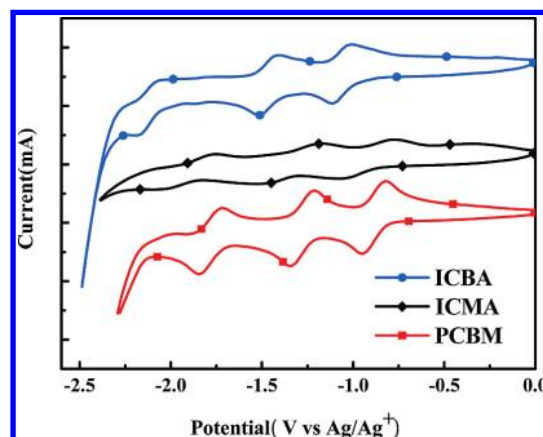

Figure 4. Cyclic voltammograms of PCBM (red line), ICMA (black line), and ICBA (blue line) in a mixed solution of *o*-dichlorobenzene/acetonitrile (5:1) with 0.1 M TBAPF$_6$ at 100 mV/s.

Table 1. Half-Wave Potentials of the Reduction Processes, Onset Reduction Potentials, and LUMO Energy Levels of ICMA, ICBA, and PCBM

C_{60} derivative	E_1 (V)[a]	E_2 (V)	E_3 (V)	E_{red}^{on}(V)/LUMO (eV)
ICMA	−0.93	−1.34	−1.90	−0.85/−3.86
ICBA	−1.07	−1.46	−2.12	−0.97/−3.74
PCBM	−0.88	−1.28	−1.78	−0.80/−3.91

[a] Potential values are versus Ag/Ag$^+$ reference electrode.

The results indicate that the addition of indene on C_{60} induces stronger absorbance of the molecule in the visible region, and ICBA could be a better photovoltaic acceptor material than PCBM from the viewpoint of visible absorption.

Electrochemical Properties of ICMA and ICBA. Electrochemistry is one of the most important properties for fullerenes.[38] Therefore, we studied the electrochemical properties of ICBA and ICMA by cyclic voltammetry. Figure 4 shows the cyclic voltammograms of ICMA and ICBA, with the cyclic voltammogram of PCBM shown for comparison. The C_{60} derivatives exhibit three well-defined, quasi-reversible reduction waves respectively in the negative potential range from 0 to −2.5 V vs Ag/Ag$^+$. The half-wave potentials (defined as $E =$

$0.5[E_{p,c} + E_{p,a}]$, where $E_{p,c}$ is the cathodic peak potential and $E_{p,a}$ is the corresponding anodic peak potential) of the reduction processes of the three molecules are listed in Table 1. It can be seen that the first (E_1), second (E_2), and third (E_3) reduction potentials all shifted negatively from PCBM to ICMA to ICBA. E_1 is shifted from −0.88 V for PCBM to −0.93 V (shifted by −0.05 V) for ICMA and to −1.07 V (shifted by −0.19 V) for ICBA, E_2 is shifted from −1.28 V for PCBM to −1.34 V (shifted by −0.06 V) for ICMA and to −1.46 V (shifted by −0.18 V) for ICBA, and E_3 is shifted from −1.78 V for PCBM to −1.90 V (shifted by −0.12 V) for ICMA and to −2.12 V

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(shifted by −0.34 V) for ICBA. Interestingly, the potential negative shift values of the indene bisadduct ICBA are about 3 times those of the indene monoadduct ICMA for all the three reduction potentials, and the values of the potential negative shift of the third reduction potential is double the values of the potential negative shifts of the first and second reduction potentials for the indene monoadduct and bisadduct. The results indicate that indene addition on C$_{60}$ results in a negative shift of the reduction potentials, and the second addition of indene on C$_{60}$ in ICBA induces a stronger negative shift of the reduction potential of the C$_{60}$ derivatives.

The onset reduction potentials of PCBM, ICMA, and ICBA were −0.80, −0.85, and −0.97 V vs Ag/Ag$^+$, respectively, which are also shown in Table 1. From onset reduction potentials, the LUMO energy levels of the molecules were calculated according to the equation[39] LUMO = −e(E_{red}^{on} + 4.71), where E_{red}^{on} is the onset reduction potential in volts vs Ag/Ag$^+$. The LUMO energy levels of PCBM, ICMA, and ICBA calculated in this way are −3.91, −3.86, and −3.74 eV, respectively. The LUMO level of ICBA is raised by 0.17 eV in comparison with that of PCBM. The higher LUMO energy level of ICBA is desirable for higher open-circuit voltage of the PSCs with ICBA as acceptor. In addition, in comparison with the 0.10 eV increase of the LUMO energy level of bisPCBM over PCBM,[35] the LUMO level of ICBA is further increased by 0.07 eV over bisPCBM, indicating that the bisadduct of indene on C$_{60}$ is more efficient at raising the LUMO energy level of the C$_{60}$ derivatives than bisPCBM.

Photovoltaic Properties of ICMA and ICBA. ICMA and ICBA were used as acceptors to fabricate bulk-heterojunction PSCs with commercial P3HT as donor, and the weight ratio of the donor to acceptor was 1:1 (see Experimental Section for details). For comparison, the PSC device based on P3HT/PCBM was also made with commercial PCBM (Nano-C, used as received) as the acceptor. The current density−voltage ($J-V$) curves of the three devices under the illumination of AM1.5G, 100 mW/cm^2 are shown in Figure 5a, and the results of 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 0.58 V for the PCBM-based device to 0.63 V for the ICMA-based device and to 0.84 V for the ICBA-based PSC. The V_{oc} of the ICBA-based device increases by ca. 45% in comparison with that of the PCBM-based device. Obviously, the V_{oc} increment of the ICBA-based PSC benefits from the higher LUMO energy level of ICBA, because it is well known that the V_{oc} of the PSCs is proportional to the difference between the HOMO of the donor (here P3HT) and the LUMO of the acceptor. The fill factor (67%) of the ICBM-based device is also increased over that (62%) of the PCBM-based device. Although there is about 10% loss of J_{sc}, from 10.8 mA/cm^2 for the PCBM-based device to 9.67 mA/cm^2 for the ICBA-based device, the significant increase in V_{oc} combined with the higher fill factor (67%) leads to a higher PCE of 5.44% for the ICBA-based PSC, which is a 40% increase in comparison with the PCE of 3.88% for the traditional PCBM-based device. The photovoltaic results for ICBA agree with and are a little better than those reported in a patent.[40] In comparison with the photovoltaic performance of the P3HT/bisPCBM solar cell with a V_{oc} of 0.73 V and PCE of 4.5%,[35]

(39) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800.
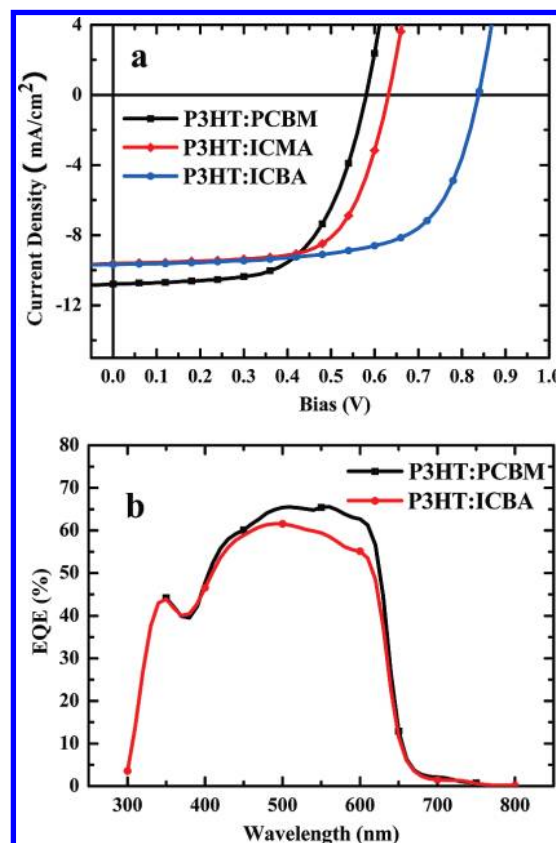(40) Laird, D. W.; Stegamat, R.; Richter, H.; Vejins, V.; Scott, L.; Lada, T. A. Patent WO 2008/018931 A2.

Figure 5. (a) Current density−voltage curves and (b) external quantum efficiencies (EQEs) of the PSCs based on P3HT as donor and the C$_{60}$ derivatives as acceptor with weight ratio of 1:1.

Table 2. Photovoltaic Performance of the P3HT-Based PSCs with Different Acceptors

acceptor	V_{oc} (V)	I_{sc} (mA/cm^2)	FF	PCE (%)
PCBM	0.58	10.8	0.62	3.88
ICMA	0.63	9.66	0.64	3.89
ICBA	0.84	9.67	0.67	5.44

the P3HT/ICBA device shows even higher V_{oc} and PCE values. If the current of the ICBA-based device can be improved to the same level as that of the PCBM-based device by optimizing the device fabrication process, efficiency >6% will be expected. The results indicate that the photovoltaic performance of ICBA as acceptor blended with P3HT is significantly superior to that of the traditional PCBM.

External quantum efficiencies (EQEs) of the devices based on PCBM and ICBA are shown in Figure 5b. High EQEs were observed in both devices, suggesting that the photon−electron conversion processes are rather efficient. The EQE value of the ICBA-based PSC is slightly lower than that of the PCBM-based PSC (which is consistent with the slightly lower I_{sc} of the ICBA-based device), in the range 450−650 nm, which is the absorption range of P3HT. The EQE result indicates that the contribution of P3HT in the ICBA-based device to I_{sc} is slightly smaller than that in the PCBM-based device.

Conclusions

The new C$_{60}$ derivative ICBA is easier to synthesize and readily soluble in common organic solvents and possesses a higher LUMO energy level than PCBM. The V_{oc} and PCE of the P3HT-based PSCs with ICBA as acceptor reached 0.84 V and 5.44%, respectively, under the illumination of AM1.5, 100

mW/cm^2, which is significantly improved in comparison with the V_{oc} of 0.58 V and PCE of 3.88% of the device with PCBM as acceptor at the same experimental conditions. ICBA is an alternative acceptor material and could be widely used in high-performance PSCs.

Supporting Information Available: Complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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