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Highly Efficient Inverted Polymer Solar Cells Based on an Alcohol Soluble Fullerene Derivative Interfacial Modification Material

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ABSTRACT: A phosphate group-containing bisadducts fullerene derivative bis-[6,6]-phenyl-C₆₀-pentyl phosphoric diethyl ester (B-PCPO) has been developed as an indium tin oxide (ITO) interlayer material in inverted polymer solar cells. The B-PCPO possessed good alcohol solubility, n-type nature, good electron transporting ability, and ITO modification function simultaneously, and it was utilized as an ITO interlayer in solution-processed multilayer inverted bulk-heterojunction polymer solar cells to improve the electron transporting and collection. It was found that the B-PCPO interlayer could effectively decrease the work function of ITO and thereby enhance the electron collection of ITO electrode. The device studies showed that the resulting solar cells' efficiencies were significantly increased from 4.83% to 6.20% by using a B-PCPO interlayer, benefiting from the dramatic enhancement in open circuit voltage and moderate increase in fill factor. Our results provide a promising approach to improve the performance of inverted polymer solar cells.

KEYWORDS: inverted polymer solar cells, alcohol soluble fullerene derivative, interfacial modification, ITO interlayer

INTRODUCTION

Bulk-heterojunction polymer solar cells (PSCs) based on a nanoscale phase separated blend of semiconducting conjugated polymer electron donor and fullerene derivative electron acceptor is one of the most promising photovoltaic technologies to directly convert the terrestrial solar radiation into electricity, owing to their mechanical flexibility and their compatibility with low-cost, large-scale fabrication by solution processing.¹⁻³ The most widely used device configuration of PSCs is the so-called sandwich structure, where the blended organic active layer was sandwiched between a low work function metal electron collecting electrode and a holecollecting poly(3,4-ethylenedioxylenethiophene):poly-(styrenesulfonic acid) (PEDOT:PSS) coated indium tin oxide (ITO) electrode.⁴ In recent years, significant improvements in power conversion efficiencies (PCEs) of PSCs with this conventional device structure have been achieved by the combined efforts from various aspects including the development of new narrow-band gap conjugated polymers and new fullerene-based acceptor materials, 5^{-10} the usage of new device processing methods,¹¹⁻¹³ the invention of innovative device structures, $^{14-16}$ the incorporation of effective interlayers, $^{17-21}$ and so on.

Compared to conventional PSCs, inverted PSCs (i-PSCs) have attracted increasing attention because of their greatly improved device stability by using air stable metals as the hole collecting electrode and ITO as the electron collecting electrode.^{15,16} To achieve highly efficient i-PSCs, it is critical to improve the electron collection of ITO electrode, as well as suppress its hole collection, since ITO is commonly used as the electron collecting electrode in i-PSCs. To realize this, many efforts were thus devoted to modify the interface between ITO and organic active layer,^{22–30} including the insertion of Cs₂CO₃ to reduce the ITO work function,²⁵ and the incorporation of semiconducting n-type metal oxides such as zinc oxide $(ZnO)^{26-29}$ and titanium oxide $(TiO_x)^{30}$ to selectively collect electrons. However, the requirement of high vacuum for the deposition of a Cs₂CO₃ layer is not compatible with the large-scale solution processing techniques, while the electrical

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Scheme 1. Chemical Structure and Synthetic Route of B-PCPO^a



"Reagents and conditions: (i) EtONa, EtOH, reflux, 6 h; (ii) NaOH, EtOH, reflux, 4 h; (iii) *p*-toluene-sulfonyl hydrazide, MeOH, reflux, 10 h; (iv) MeONa, pyridine, 30 min; C_{60} , 75 °C, 16 h; and then reflux 24 h; (v) BBr₃, *o*-DCB, 0 °C, then room temperature, overnight; (vi) triethyl phosphite, *o*-DCB, reflux, 24 h.

properties of an n-type metal oxide layer are sensitive to the surface adsorption of oxygen, UV-irradiation, and processing conditions, which limited the widespread application of these materials in i-PSCs.³¹⁻³³

Alternatively, organic interface modification materials have also attracted great attention for i-PSCs, mainly due to their solution processability and successful applications in polymer light-emitting diodes as electron injection layers.^{20,34-41} For example, hydrophilic polymers (HPPs) (such as poly(ethylene oxide) (PEO)^{38,39} and alcohol soluble polyfluorenes and polycarbazoles $^{39-41}$), which have orthogonal solubilities relative to the above active layer to allow for the fabrication of solutionprocessed multilayer devices without interface mixing, were used as an independent interlayer or TiO_x/HPP complex interlayer on top of ITO in i-PSCs. Moreover, the work function of ITO can be effectively decreased by spin-coating a thin layer of HPPs on top of it, 41^{-43} which finally led to better device performances. Alternatively, these HPPs are not ideal candidates for ITO modification in i-PSCs in principle because of the insulating nature of PEO, and the p-type nature of alcohol soluble polyfluorenes and polycarbazoles, which are unfavorable for electron transporting and collection in the ITO electrode. However, cross-linked fullerene materials, which are n-type in nature, were reported as effective electron transporting layers (ETLs) on top of ZnO or TiO_x in i-PSCs.⁴⁴⁻⁴⁶ Despite of having a remarkably high PCE of 6.2% achieved by this mean, these cross-linked fullerene materials cannot be used as an independent ITO interlayer, and a layer of n-type semiconducting metal oxides is indispensable due to the poor alignments between the LUMO levels of these fullerene-based materials (\sim 3.9 eV) and the work function of ITO (\sim 4.3-4.7 eV), which complicated the device fabrication.

In this contribution, we developed a new alcohol soluble fullerene material, bis-[6,6]-phenyl- C_{60} -pentyl phosphoric diethyl ester (B-PCPO), which integrated the benefits of both HPPs (good alcohol processability and ITO modification function) and fullerene-based interfacial materials (n-type nature and good electron transporting ability), as an independent ITO interlayer in i-PSCs. It was found that the work function of ITO was effectively decreased by spin-coating

a single layer of B-PCPO on top of ITO. Consequently, the resulting devices' PCEs were significantly enhanced from 4.83% to 6.20% when a carbazole-derived copolymer PCDTBT⁴⁷ and [6,6]-phenyl C_{71} butyric acid methyl ester (PC₇₁BM) were used as donor and acceptor, respectively. Our results showed that alcohol soluble fullerene material B-PCPO is promising as an independent ITO interlayer for i-PSCs.

RESULTS AND DISCUSSION

Synthesis and Characterization. The chemical structure and synthetic route of B-PCPO were demonstrated in Scheme 1. To ensure sufficient alcohol solubility of the resulting fullerene-based material, bisadduct C₆₀ derivative containing two pendant phosphate groups was designed and synthesized. Note that bisadduct C₆₀ derivative is a mixture of a series of regioisomers, which have similar electronic properties and can be directly used for device fabrication without time-consuming separation.^{48,49} Compound 5, which is a key intermediate to provide 1,3-dipoles for the following [3 + 2] cycloaddition reaction to C₆₀, was synthesized by a three-step procedure, i.e., nucleophilic substitution from compound 1 and 2 to yield compound 3, elimination from β -benzoylacetic ester 3 to yield ketone 4, which was converted to tosylhydrazone 5 via an addition-elimination process. The introduction of side chains onto C_{60} was performed by using [3 + 2] cycloaddition from compound 5 to C_{60} and then underwent a thermal isomerization to yield compound 6. The protect groups of p-cresoxyl in compound 6 were cleaved by BBr3 under mild conditions to give side chain bromo-functionalized intermediate 7 in a high yield. The target compound B-PCPO was thus obtained by treating compound 7 with triethyl phosphite in o-DCB at 140 °C, and the product was purified by column chromatography. The product was characterized by ¹H NMR, and fast atom bombardment mass spectrometry (FAB-MS). The B-PCPO was readily soluble in high polarity solvent, such as methanol, ethanol, i-propanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), etc. Hence, B-PCPO would be a suitable candidate as ETL material for fabricating multilayer i-PSCs devices with orthogonal solvents.

Electrochemical Properties. The electrochemical property of B-PCPO thin film was studied by cyclic voltammetry, and the resulted cyclic voltammogram is shown in Figure 1. For



Figure 1. Cyclic voltammograms of (a) $PC_{61}BM$, (b) $PC_{71}BM$, and (c) B-PCPO as thin films.

comparison, the cyclic voltammogram of [6,6]-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) and PC₇₁BM were also recorded under the same conditions. PC61BM and PC71BM exhibited three well-defined n-doping processes in the scanning range from 0 to -1.8 V, while B-PCPO exhibited two welldefined reduction processes in the scanning range from 0 to -1.6 V. From the reduction curves, the onset potentials of each reduction process were evaluated to be -0.73, -0.96, and -1.40 V for PC₆₁BM, -0.79, -0.97, and -1.28 V for PC₇₁BM, and -0.63 and -0.97 V for B-PCPO, respectively. The reference electrode was calibrated by the ferrocene/ferrocenium (Fc/Fc+) (4.8 eV below vacuum level)⁵⁰ to obtain accurate energy levels. The LUMO levels of PC₆₁BM, PC₇₁BM, and B-PCPO were thus calculated to be -3.75, -3.69, and -3.85 eV, respectively. Notably, the LUMO level of B-PCPO is slightly lower than those of PC₆₁BM and PC₇₁BM. This phenomenon is different from the fact that bisadduct C_{60} derivatives usually possess an elevated LUMO level compared to monoadduct C_{60} derivatives,^{10,48,49} suggesting that the polar side chains may have some influence on the electrochemical properties of the resulting fullerene derivatives. Nevertheless, the well-aligned LUMO energy levels between PC₆₁BM/ PC71BM and B-PCPO indicate that B-PCPO would be a good electron transporting material in i-PSCs.

Photovoltaic Performances and Interfacial Modification Functions. I-PSCs were fabricated with the configuration of ITO/interlayer/PCDTBT:PC₇₁BM/MoO₃/Al to study the interfacial function of B-PCPO. The chemical structure of donor polymer (PCDTBT) and acceptor ($PC_{71}BM$), the device configuration, and the energy levels of the component materials in the device are presented in Scheme 2. A 5 nm layer of B-





^{*a*}The energy level values for B-PCPO, $PC_{71}BM$, and PCDTBT were determined by cyclic voltammetry in our lab under the same conditions. The work function of ITO was estimated by XPS. The work function of Al and the band structure of MoO_3 were from refs 51 and 52.

PCPO was deposited on top of ITO from its ethanol solution as an interlayer. For comparison, control devices using sol–gel processed ZnO interlayer²⁶ with thickness of 40 nm and without interlayer were also fabricated under the same conditions.

The current density–voltage (J-V) curves of the solar cells measured under AM 1.5G irradiation (84 mW cm⁻²) are presented in Figure 2. The corresponding J_{sc} , V_{oc} , FF, and PCE values as determined from the J-V curves are summarized in Table 1. The best i-PSC with bare ITO electrode showed a PCE value of 4.83%, with a J_{sc} of 10.2 mA cm⁻², a V_{oc} of 0.71 V, and a FF of 56.1%. After inserting a thin layer of sol–gel processed ZnO as ETL, the device's PCE reached 5.31% with a significantly enhanced V_{oc} of 0.95 V, a fairly improved FF of



Figure 2. J-V characteristics of inverted PCDTBT:PC₇₁BM solar cells without interlayer, and with ZnO or B-PCPO interlayer.

Table 1. Photovoltaic Performan	ce Parameters of Best Inverte	ed PCDTBT:PC ₇₁ BM Solar	Cells without Inter	ayer and with ZnO
or B-PCPO Interlayer ^a				

interlayer	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}~({ m V})$	FF (%)	PCE (%)	$R_{\rm sh}~(\Omega~{\rm cm}^2)$	$R_{\rm s}~(\Omega~{\rm cm}^2)$		
B-PCPO	$9.50 \ (9.32 \pm 0.23)$	$0.89~(0.87~\pm~0.02)$	$61.7 (58.6 \pm 0.2)$	$6.20 (5.65 \pm 0.35)$	4.2×10^{4}	3.3		
ZnO	$8.14~(8.55~\pm~0.58)$	$0.95~(0.87~\pm~0.06)$	57.8 (55.9 \pm 0.3)	$5.31 (4.96 \pm 0.32)$	9.1×10^{4}	3.8		
no interlayer	$10.2 (9.01 \pm 0.90)$	$0.71~(0.64~\pm~0.04)$	$56.1 (53.2 \pm 0.4)$	$4.83 (3.66 \pm 0.73)$	7.2×10^{4}	11		
ethanol washed	$9.86 \ (9.53 \pm 0.24)$	$0.65~(0.60~\pm~0.04)$	57.4 (52.8 \pm 0.3)	$4.31 (3.58 \pm 0.53)$	6.0×10^{4}	15		
^a Values inside the parentheses were average values, and the corresponding standard deviations were calculated over eight devices.								

57.8%, but a noticeably decreased J_{sc} of 8.14 mA cm⁻². Interestingly, the i-PSC using B-PCPO as the ITO interlayer delivered comparable performance as the device using ZnO as the interlayer. The B-PCPO/ITO electrode device offered a higher PCE of 6.20%, with a J_{sc} of 9.50 mA cm⁻², a V_{oc} of 0.89 V, and a FF of 61.7%. Notably, V_{oc} and FF of the ITO/B-PCPO device were simultaneously enhanced relative to the bare ITO electrode device, which led to higher overall performance even though I_{sc} was slightly decreased. It is interesting that B-PCPO exhibited comparable performance as an ETL material relative to the solution processed ZnO, making it a good alternative ETL material in i-PSC device design. To distinguish between the solvent effect on ITO and the effect on ITO introduced by B-PCPO ETL alone, the reference i-PSC devices using ethanol washed ITO electrode were fabricated, and the results are also listed in Table 1. The statistical data (average values and standard deviations) of photovoltaic performances calculated from eight repeating devices for each kinds of i-PSCs are also listed in Table 1. It was clearly shown that the ITO/B-PCPO devices exhibited significantly improved device performances compared to bare ITO devices, while the EtOH solvent did not play a role on the improved device performances of the resulting devices. In addition to routine device characterizations, the light soaking effect, which is a common problem in i-PSCs, was also investigated in this study.^{53,54} This effect typically leads to great changes in device performances after UV irradiation. However, it was found that the light soaking effect was insignificant for the i-PSC devices using ZnO or B-PCPO as ETL in our study. We irradiated the as-prepared ITO/ZnO and ITO/B-PCPO i-PSC devices with 365 nm UV light for 10 min, and little difference in device performance was observed. The results are shown in the Table S1 in Supporting Information.

To gain an in-depth understanding of the improvement of device performance after inserting the B-PCPO ETL, the external quantum efficiency (EQE) spectra (see Figure 3) of the i-PSCs both with and without ETLs were measured. The J_{sc}



Figure 3. EQE spectra of inverted PCDTBT:PC₇₁BM solar cells without interlayer and with ZnO or B-PCPO interlayer.

of three i-PSC devices agreed well with the integration of the corresponding EQE spectra. The shape of the EQE curve of the ITO/B-PCPO device was almost identical with that of the bare ITO device across the entire wavelength range, despite that a slight decrease in values was observed. However, the ITO/ZnO device exhibited significant loss in EQE in two wavelength regions (400-435 nm and 480-620 nm), which was consistent with the relative low J_{sc} of ITO/ZnO devices with respect to the other two kinds of devices. Considering the good transparence of ZnO in the wavelength range over 400 nm, the EQE loss of the ITO/ZnO device is possibly caused by the charge carrier recombination at the interface or the change in active layer morphology due to the insertion of the ZnO interlayer. The surface of metal oxides processed by the sol-gel method usually has hydroxyl groups,⁵⁵ which can introduce charge trapping at the metal oxide/active layer interface, leading to high interface charge recombination. Besides, it is well-known that the underlying interfacial layer has significant influence on the overlayer BHJ morphology.^{17,56-60} For example, Jen's group has reported that the use of metal oxide directly or after being modified by a fullerene-based self-assembled monolayer as ITO interlayers in i-PSCs led to different surface roughness for the above active layer, as well as different BHJ phase separation and crystallinity. 60 To study the influence of the interfaical layers on the morphology of overlying BHJ layer as well as to better understand the difference of photocurrent and EQE spectra of different solar cell devices, atomic force microscope (AFM) under the tapping mode was used to track the surface morphologies of the PCDTBT:PC71BM layer on different substrates, and the corresponding images were presented in Figure 4. The surface of the PCDTBT:PC71BM layer on top of bare ITO or ITO/B-PCPO were both very smooth and homogeneous, with near root-mean-square (rms) roughnesses of 0.79 and 0.78 nm, respectively. On the contrary, the film of PCDTBT:PC71BM on top of ITO/ZnO exhibited significantly larger surface roughness due to the zigzag features of the underlying ZnO layer. Correspondingly, the rms roughness of the PCDTBT:PC71BM layer was 3.35 nm, which is much higher than those of the films on top of bare ITO and ITO/B-PCPO. The more uniform film of PCDTBT:PC71BM on top of bare ITO and ITO/B-PCPO were beneficial for obtaining as large as heterojunction interface areas, which is also consistent with the J_{sc} and EQE spectra observed for the related solar cell devices.

The J-V characteristics of the devices obtained under dark conditions are shown in Figure 5. Clearly, the ITO/B-PCPO device and ITO/ZnO device exhibited similar J-V characteristics under dark conditions. In the region from -2 to 0.95 V, the reverse and leakage currents of the inverted devices using B-PCPO and ZnO as interlayer were significantly suppressed compared to that of the bare ITO electrode device. Such reduced dark leakage current is beneficial for $V_{\rm oc}$ and PCE improvements in PSC devices.⁶¹ While in the region over 0.95



Figure 4. Tapping mode surface topographic AFM images of the PCDTBT:PC₇₁BM (1:4) layer on top of (a) bare ITO, (b) ITO/B-PCPO, and (c) ITO/ZnO.



Figure 5. Dark currents of inverted PCDTBT:PC₇₁BM solar cells without interlayer and with ZnO or B-PCPO interlayer.

V, the B-PCPO and ZnO interlayer devices showed higher injection currents compared to that of the bare ITO electrode device, which is indicative of increased electron injection from the ITO electrode and is consistent with the decreased series resistance (R_s) (11, 3.8, and 3.3 Ω cm² for bare ITO, ITO/ZnO, and ITO/ZnO devices, respectively) (see Table 1).⁶² The improved diode characteristics of the ITO/B-PCPO device and the ITO/ZnO device compared to that of the control bare ITO electrode device suggested that B-PCPO is as efficient as ZnO in blocking holes and collecting electrons, and thereby contributed to the improved photovoltaic performance. In addition, the reduced leakage currents and series resistances in devices with an interlayer are beneficial for obtaining a higher V_{oc} due to the reduced potential drop across the devices.

To gain an in-depth understanding of the origin of the significant enhancement in V_{oc} of i-PSCs with a B-PCPO interlayer compared to that of the control bare ITO electrode device, the work function or surface potential of ITO substrates before and after modification by B-PCPO were measured by Xray photoelectron spectroscopy (XPS).^{63,64} The XPS secondary electron cutoff of the ITO substrates without O2 plasma treatment as used in actual i-PSC devices are presented in Figure 6. The work functions were measured to be 4.3 and 3.9 eV for a pristine ITO substrate and B-PCPO coated ITO, respectively. Clearly, the work function of ITO can be decreased by ~0.4 eV via the introduction of a thin B-PCPO layer, which may be caused by the dipole formation in the ITO/active layer interface as the function of many other hydrophilic polymers in optoelectronic devices.^{41,43} The lowered work function of ITO is beneficial for enhancing the built-in potential in i-PSCs, which in turn contributed to the enhanced V_{oc} . ^{65,66} The decreased work function of ITO by B-PCPO interlayer can also offer better energy level alignment with the LUMO level of PC71BM and thereby facilitate the



Figure 6. Comparison of XPS secondary cutoff of ITO substrates with a B-PCPO layer and without thin film on top.

electron transporting and collection, which in turn transform to the enhancement in FF. To distinguish between the solvent effect on ITO and the effect on ITO introduced by B-PCPO ETL alone, the XPS work function measurements for bare ITO, EtOH covered ITO, and B-PCPO covered ITO after O_2 plasma were also conducted. As the results shown in Figure S2 in the Supporting Information, no work function change can be observed.

CONCLUSIONS

In conclusion, an n-type, alcohol soluble, electron-transporting fullerene bisadduct B-PCPO containing polar side chains was synthesized and utilized as an efficient ITO interlayer to improve the electron transporting and collection in high performance i-PSCs. By using B-PCPO as ETL on top of ITO, the PCE values of the i-PSCs can be increased from the initial 4.83% to 6.20%, benefiting from the dramatic enhancement in $V_{\rm oc}$ and moderate increase in FF. The improvement in device performances were revealed to be mainly caused by the decrease of the ITO work function. Much higher PCE values would be achievable if a more efficient photoactive system was used to fabricate solar cells. Moreover, our results indicated that B-PCPO is comparable to sol-gel processed ZnO as ETL in i-PSCs based on the same BHJ system. Combining ideal energy levels, excellent electron transporting/collection ability, and good alcohol solubility, hydrophilic fullerene derivatives would be a promising family of interfacial materials for highly efficient i-PSCs.

EXPERIMENTAL SECTION

Instruments and Measurements. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-300 spectrometer operating at 300 or 75 MHz, respectively, in deuterated chloroform or deuterated dimethyl sulfoxide solution at room temperature and were referred to tetramethylsilane. Mass spectrometry (MS) data of compounds 3– 5 were obtained on a Bruker Esquire HCT PLUS with atmospheric pressure chemical ionization resource (APCI). The remaining MS data were collected with fast atom bombardment (FAB) MS on a MAT 95XP (Thermo). UV–vis absorption spectra were recorded on an HP 8453 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI800C electrochemical workstation with a platinum working electrode and a Pt wire counter electrode at a scan rate of 30 mV s⁻¹ against a reference electrode of saturated calomel electrode (SCE) with an argon-saturated anhydrous solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. The films of fullerene materials for electrochemical measurements were coated from their dilute solution.

Materials. Benzoylacetic ester (1) was purchased from Aladdin Reagent Inc. *p*-Cresoxypropyl bromide (2) was prepared according to a literature reported method.⁶⁷ The other chemical reagents, unless otherwise specified, were purchased from Alfa Aesar or Sigma-Aldrich and used as received. All the solvents used were further purified prior to use.

Synthesis of 3-(p-Cresoxypropyl)benzoylacetic Ester (3). Benzoylacetic ester (1) (20 g, 52.1 mmol) and p-cresoxypropyl bromide (2) (5.96 g, 26 mmol) were dissolved in 15 mL of absolute alcohol. After degassing with argon for 15 min, sodium ethoxide (0.177 g, 26 mmol) was added into the solution. The reaction mixture was refluxed for 6 h under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure, water was added, and the mixture was extracted with dichloromethane three times. The combined organic layers were washed with water and brine sequentially and then dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the residue was purified using column chromatography (silica gel, petroleum ether/ethyl acetate (15/1)) to afford compound 3 as a colorless oil (4.4 g, 50%). ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 8.02–7.99 (d, J = 7.17Hz, 2H), 7.60–7.56 (t, J = 4.14 Hz, 1H), 7.50–7.45 (t, J = 7.8 Hz, 2H), 7.08–7.05 (d, J = 8.31 Hz, 2H), 6.79–6.75 (d, J = 6.63 Hz, 2H), 4.46-4.41 (t, J = 7.2 Hz, 1H), 4.19-4.12 (q, J = 7.08 Hz, 2H), 4.00-3.96 (t, J = 6.42 Hz, 2H), 2.28 (s, 3H), 2.25-2.17 (m, 2H), 1.91-1.86 (m, 2H), 1.20–1.15 (t, J = 7.11 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 195.14, 169.90, 156.67, 136.18, 133.54, 129.88, 128.76, 128.66, 114.30, 67.32, 61.43, 53.78, 27.15, 25.83, 20.47, 14.02. MS (APCI, +MS): m/z = 341.2.

Synthesis of 4-(p-Cresoxybutyl)phenyl Ketone (4). To a 250 mL two-necked round-bottom flask, compound 3 (13.2 g, 38.8 mmol), sodium hydroxide (1.86 g, 46.6 mmol), and absolute alcohol (110 mL) were added under argon atmosphere. The reaction mixture was stirred for 4 h under reflux. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane three times. The combined organic phases were washed with water and brine, sequentially, and then dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the residue was purified using silica gel column chromatography and then recrystallized from methanol to yield compound 4 as colorless needles (7.5 g, 72%). ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 7.98–7.96 (d, J = 7.05Hz, 2H), 7.59-7.53 (t, J = 6.06 Hz, 1H), 7.49-7.43 (t, J = 6.21 Hz, 2H), 7.08-7.06 (d, J = 4.44 Hz, 2H), 6.80-6.78 (d, 2H), 4.01-3.97 (t, J = 6.09 Hz, 2H), 3.08 (t, J = 6.81 Hz, 2H), 2.28 (s, 3H), 1.96-1.85 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 200.02, 156.87, 137.04, 132.94, 129.85, 128.57, 128.04, 114.39, 67.67, 38.12, 29.69, 28.87, 20.98, 20.44. MS (APCI, +MS): m/z = 269.1.

Synthesis of 4-(p-Cresoxybutyl)benzoyl p-Tosylhydrazone(5). To a 250 mL two-necked round-bottom flask, compound 4 (4.87 g, 18.2 mmol), p-toluene-sulfonyl hydrazide (4.06 g, 21.8 mmol), catalytic amount of HCl, and methanol (100 mL) were added under argon atmosphere. The reaction mixture was stirred and refluxed for 10 h under argon atmosphere. After cooling to room temperature, the reaction mixture was placed into a fridge and frozen at -25 °C overnight. The resulting white precipitate was collected by filtration and washed with cool methanol. The crude product was further purified by recrystallizing from methanol twice to afford the title compound as colorless needles (7.04 g, 89%). ¹H NMR (d_6 -DMSO, 300 MHz), δ (ppm): 10.71 (s, 1H), 7.70–7.78 (d, J = 8.25 Hz, 2H), 7.61–7.58 (m, 2H), 7.41–7.33 (m, 5H), 7.07–7.05 (d, J = 8.16 Hz, 2H), 6.80–6.76 (d, J = 8.55 Hz, 2H), 3.91–3.87 (t, J = 6.36 Hz, 2H), 2.76–2.71 (t, J = 7.83 Hz, 2H), 2.36 (s, 3H), 2.21 (s, 3H), 1.74–1.67 (m, 2H), 1.53–1.48 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 156.93, 156.18, 143.76, 137.01, 136.75, 130.23, 129.96, 129.72, 129.49, 128.89, 127.89, 126.60, 114.77, 67.46, 28.92, 26.66, 22.75, 21.46, 20.52. MS (APCI, +MS): m/z = 436.6.

Synthesis of Bis-[6,6]-phenyl-C₆₁-pentyl p-Tolyl Ether (6). To a 100 mL two-necked round-bottom flask, compound 5 (700 mg, 1.6 mmol), sodium methoxide (90 mg, 1.67 mmol), and dry pyridine (10 mL) were added under argon atmosphere. The mixture was stirred at room temperature for 30 min. To the mixture, a solution of C_{60} (925 mg, 1.28 mmol) in o-DCB (45 mL) was added, and the reaction mixture was stirred at 75 °C under argon for 16 h. Afterward, the solution was further heated, and the reaction mixture was allowed to be stirred and refluxed for 24 h under argon atmosphere. After cooling to room temperature, the reaction mixture was precipitated from methanol. After drying, the resulted precipitates were dissolved in toluene and reabsorbed on silica gel. The unreacted C_{60} , [6,6]-phenyl-C₆₁-butyl *p*-tolyl ether, and bis-[6,6]-phenyl-C₆₁-butyl *p*-tolyl ether were separated by column chromatography (silica gel, petroleum ether/toluene (5/1)). The title compound 6 was precipitated with methanol, centrifuged, and decanted. The product was treated with the same manner for several times to yield a brown solid (483 mg, 31%). ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 8.01–7.80 (m, 4H), 7.55– 7.43 (m, 6H), 7.05-7.03 (m, 4H), 6.82-6.70 (m, 4H), 4.04-3.76 (m, 4H), 3.14-2.78 (m, 4H), 2.28-2.24 (m, 6H), 2.06-1.95 (m, 8H). MS (FAB): m/z = 1224.

Synthesis of Bis-[6,6]-Phenyl-C₆₁-pentyl Bromide (7). To a solution of compound 6 (510 mg, 0.417 mmol) in *o*-DCB (40 mL) at 0 °C was added BBr₃ (3 mL) dropwise under argon atmosphere. The reaction mixture was slowly warmed to room temperature and kept stirred for 4 h. Then, water was added to quench the reaction. After washing with water for several times, the separated organic phase was precipitated from methanol. The collected precipitate was purified using column chromatography (silica gel, petroleum ether/toluene (5/1)). The solution of pure title compound 7 was concentrated and precipitated from methanol to a brown solid (453 mg, 93%). ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 8.13–7.76 (m, 4H), 7.69–7.40 (m, 6H), 3.57–3.42 (m, 4H), 3.09–2.74 (m, 4H), 2.18–2.00 (m, 8H). MS (FAB): m/z = 1171.

Synthesis of Bis-[6,6]-phenyl- C_{61} -pentyl Phosphoric Diethyl Ester (8). To a 50 mL two-necked round-bottom flask, compound 7 (300 mg, 0.26 mmol), the excess triethyl phosphite (1 mL), and *o*-DCB (15 mL) were added under argon atmosphere. The reaction mixture was heated to 140 °C for 24 h. After cooling to room temperature, the mixture was subjected to a silica gel column and eluted with toluene/ alcohol (10/1). The solution of title compound 8 was concentrated and precipitated from hexane to yield a brown solid (273 mg, 83%). ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 8.12–7.74 (m, 4H), 7.65–7.38 (m, 6H), 4.07 (m, 8H), 3.07–2.55 (m, 4H), 1.75 (m, 12H), 1.36–1.26 (m, 12H). MS (FAB): m/z = 1285.

Device Fabrication and Characterization. The inverted polymer solar cell devices were fabricated by the following process. First, prepatterned ITO glass substrates were cleaned by subsequent ultrasonication in acetone, detergent, deionized water, and isopropyl alcohol. Then, the ITO was modified to function as a transparent electron collecting electrode by spin-coating a 20 nm thick B-PCPO layer onto the ITO surface. Approximately 5 nm of B-PCPO was generally left after deposition of the active layer from o-DCB/CB = 3:1 solvent mixture according to the absorption spectra. The active layer was then spin-coated onto the B-PCPO layer (PCDTBT/PC₇₁BM = 1:4 with a total concentration of 15 mg mL⁻¹ in *o*-DCB/CB = 3:1 solvent mixture) with a thickness of 80 nm. After the spin-coating of the active layer, the devices were transferred into a thermal evaporation chamber with a vacuum level of 3×10^{-6} mbar. To complete the device fabrication, 10 nm of MoO₃ and 100 nm of Al were then thermally evaporated onto the active layer to form the top electrode of the device. The devices using sol-gel processed ZnO as

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the interlayer were fabricated according to the literature reported procedures,²⁶ and the thickness of ZnO layer was 40 nm. The effective area of a single device was 0.16 cm^2 .

The PCEs of the inverted solar cell devices were measured under an AM1.5G solar simulator (Model 91192, Oriel, USA). The light intensity was calibrated before the device testing using a standard silicon solar cell, giving a value of 84 mW cm⁻². The photo and dark current density–voltage (J-V) characteristics were recorded with a Keithley 2410 and a Keithley 236 source meter, respectively. The incident-photon-to-converted current efficiency (IPCE) spectra of the i-PSCs were measured by an EQE measurement system (Model DSR-100UV-B, Zolix, Beijing).

The XPS work function measurement was carried out in an ESCALAB 250 system (Thermo-VG Scientific) using monochromatized Al K α (hv = 1486.6 eV) excitation. The measurement was carried out in ultra high vacuum (2×10^{-10} mbar). To prevent charge buildup on the sample surface, a -5 V bias was applied to the ITO substrates during measurement. The energy scale to determine the absolute values of work function was calibrated by measuring the Fermi edge of Ar ion sputtered Au, Ag, and Cu thin film samples, and the errors are within 0.1 eV.

ASSOCIATED CONTENT

S Supporting Information

High-resolution mass spectrometry of the fullerene derivatives and UV-vis absorption spectra of the fullerene materials; XPS work function data of ITO substrates with/without B-PCPO layer and ITO substrate subject to ethanol washing; i-PSC device performance before and after light-soaking. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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