Functionalized Amphiphilic Diblock Fullerene Derivatives as a Cathode Buffer Layer for Efficient Inverted Organic Solar Cells

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ABSTRACT: The amphipathic interface layer sandwiched between cathode and active layers had always played a role to balance interface compatibility and interfacial energy barriers in inverted organic solar cell (OSC) devices. Two functionalized amphipathic diblock fullerene derivatives named C_{60}-2DPE and C_{60}-4HTPB were synthesized and applied as an interface layer in modifying zinc oxide (ZnO). Based on their amphipathic characteristics, the solvent treatment was introduced to cause an obvious self-assembly of the two materials on ZnO. The introduced cathode buffer layer could improve the interface compatibility between ZnO and the organic active layer effectively with its amphipathic blocks. Based on the PTB7-Th:PC_{71}BM system, the OSC devices with a functionalized fullerene derivative layer could reach a power conversion efficiency of 9.21 and 8.86% for C_{60}-2DPE and C_{60}-4HTPB, respectively.

1. INTRODUCTION

With the advantage of high electron mobility, functionalized fullerene derivatives were one of the most used interface material in bulk heterojunction organic solar cells (OSCs). In traditional OSC devices, the most common way of fabricating the active layer was to control the ratio of donor and acceptor, and the most used acceptor was a fullerene based material. To get a high efficiency device, an interface layer (such as metal oxide) was usually introduced to decrease the interface barrier between the indium tin oxide (ITO) electrode and the organic active layer.

Based on the characteristic of low work function, zinc oxide (ZnO) was always used as a buffer layer to decrease the barrier of the cathode electrode with an ohmic contact in inverted OSCs. However, the trap sites and defects of ZnO always required an amphipathic interface material to be introduced between ZnO and the active layer to get an efficient device. Among the most commonly used interface material to modify ZnO was the amphipathic organic material, especially the functionalized amphipathic fullerene derivatives. Amphiphilic fullerene derivatives functionalized with polar groups can be regarded as hydrophobic–hydrophilic diblock molecular, in which fullerene and polar groups were the hydrophobic and hydrophilic blocks, respectively. The introduced amphiphilic diblock fullerene derivative layer can also guarantee the improvement of interface compatibility when introducing to modify ZnO in OSC devices.

Here, two functionalized amphiphilic diblock fullerene derivatives named C_{60}-2DPE and C_{60}-4HTPB were synthesized and also applied in modifying ZnO in inverted OSCs. The OSC devices composed of the PTB7-Th:PC_{71}BM active layer showed considerably improved performance by introducing the two novel materials. The inner fullerene derivative layer between ZnO and the active layer could have an obvious self-assembly under the treatment of toluene, which was also supported by the X-ray diffraction (XRD) and water contact angle measurement. Because of the multielectron transmission channels formed by the fullerene block of functionalized fullerene derivatives in the cathode interface layer, the inverted OSC devices based on the PTB7-Th:PC_{71}BM system also reached a power conversion efficiency (PCE) of 9.21 and 8.86% for C_{60}-2DPE and C_{60}-4HTPB, respectively, compared with that of 8.13% for bare ZnO. The chemical structure of PC_{71}BM, PTB7-Th, C_{60}-2DPE, and C_{60}-4HTPB and architecture of the inverted OSC device are shown in Figure 1.

2. RESULTS AND DISCUSSION

2.1. UV–Visible Absorption. The UV–visible absorption spectra of PC_{60}BA, 2DPE, 4HTPB, C_{60}-2DPE, and C_{60}-4HTPB are shown in Figure S1, and all of the UV absorption spectra were obtained in solution with materials dissolved in dimethyl sulfoxide (DMSO) with a concentration of around 0.05 mg/mL. The sharp absorption that appeared at 316 nm in the absorption of 2DPE and 4HTPB was caused by the conjugate structure, and the characteristic absorption peak of PC_{61}BA appeared at 330 and 435 nm. For C_{60}-2DPE, the wide peak that ranged from 280 to 340 nm may be caused by the strong intramolecular effect between PC_{60}BA and 2DPE. For
C$_{60}$-4HTPB, there is also a wide peak ranging from 318 to 380 nm. Compared with the characteristic absorption peaks of PC$_{61}$BA, 2DPE, and 4HTPB, the absorption spectra of C$_{60}$-2DPE and C$_{60}$-4HTPB were also evident to confirm the structure of C$_{60}$-2DPE and C$_{60}$-4HTPB.

2.2. Morphology Characterization. As presented in Figure 2, the surface topographies were measured to confirm the surface morphology of three samples. ZnO was distributed on ITO substrate uniformity with a root-mean-square (rms) of 2.67 nm, and the smooth surface of ZnO showed the well-wetting properties between ZnO and ITO. C$_{60}$-4HTPB also formed a uniformity layer on ZnO with an rms of 2.85 nm, which was due to their similar hydrophilic properties. However, C$_{60}$-2DPE formed a sharp-shaped layer on ZnO with an rms of 6.60 nm, which was caused by much aggregation of fullerene derivatives. The different surface topographies showed the discrepancy of hydrophilic properties between the two fullerene derivatives. When modifying ZnO, the amine-functionalized fullerene derivative C$_{60}$-2DPE aggregated in sharp shape with high surface roughness with the evaporation of the solvent. However, the quaternary ammonium salt-functionalized fullerene derivative C$_{60}$-4HTPB formed in uniform films on ZnO with low surface roughness, which was because of the good wetting properties with ZnO.

2.3. Self-Assembly. Based on the amphiphatic characteristics of the two fullerene derivatives, XRD and contact angle were used to test their self-assembly after the treatment of toluene. In this work, the samples were named thermal annealing (TA) and solvent annealing (SA) before and after the solvent treatment, respectively.

The diffraction peaks of the XRD spectrum can reflect the regularity of the sample surface directly. For the ITO/ZnO sample, it was interesting that there was a little difference between TA and SA samples, and in both, the diffraction peaks were weak, as presented in Figure 3a. For ITO/ZnO/C$_{60}$-2DPE and ITO/ZnO/C$_{60}$-4HTPB samples, the weak diffraction peaks of TA samples located at 30° demonstrated that fullerene derivatives on ZnO were presented in disordered distribution. However, the intensity of diffraction peaks had an obvious enhancement in the XRD spectrum of the two SA samples, which was caused by the regularity of fullerene derivatives, as shown in Figure 3b,c. Based on the conjugated rigidity and polarity difference of fullerene and conjugated fluorene blocks, self-assembly of the two fullerene derivatives was caused by the solvent treatment. When the two fullerene
derivatives ordered on ZnO, the counts of the tested diffraction peaks will be increased obviously.

The photographs of water droplets on the three samples are shown in Figure 4. The water contact angle is an important

dervative ordered on ZnO, the counts of the tested diffraction peaks will be increased obviously.

Figure 3. XRD spectrum of samples: (a) ITO/ZnO, (b) ITO/ZnO/C_{60}-4HTPB, and (c) TA ITO/ZnO/C_{60}-2DPE.

Figure 4. Water contact angle of samples: (a) TA ITO/ZnO, (b) TA ITO/ZnO/C_{60}-4HTPB, (c) TA ITO/ZnO/C_{60}-2DPE, (d) SA ITO/ZnO, (e) SA ITO/ZnO/C_{60}-4HTPB, and (f) SA ITO/ZnO/C_{60}-2DPE.

Figure 5. XPS spectra of samples ZnO and ZnO/fullerene derivatives: (a) O 1s spectra, (b) element spectra, (c) C 1s spectra, and (d) atomic concentrations of O 1s, C 1s, and Zn 2p.
index to represent the surface hydrophobicity, and small water contact angle always indicated good wetting properties between the fullerene derivatives and the ZnO layer. Water formed in droplets with contact angles of 48, 58.5, and 56° on the surface of three different TA samples, respectively. However, water also formed droplets with contact angles of 48, 62.5, and 59.5° on the surface of three different SA samples, respectively. For the ITO/ZnO sample, the unchanged water contact angle demonstrated that the surface hydrophobicity can be kept unchanged under the treatment of toluene. However, the enhancement of the water contact angle on two other SA samples with treatment of toluene supported that the surface hydrophobicity of the two samples have changed obviously, which was caused by the self-assembly of fullerene derivatives under the solvent treatment.

2.4. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) spectra of three samples are presented in Figure 5. For ITO/ZnO, the O 1s peaks of 529.8 and 531.0 eV (Figure 5a) were corresponded to the Zn=O bonds and hydroxyl oxygen, respectively. For two other samples, the new peaks (∼530.4 and 530.8 eV) appeared for C60-2DPE and C60-4HTPB, respectively, which originated from carboxyl groups (COOR). Figure 5b presented the XPS spectra of three different samples, and the element peaks of zinc (Zn), oxygen (O), stannum (Sn), indium (In), and carbon (C) were all measured on the surface of the ITO/ZnO sample. In addition, the obviously enhanced C 1s peak and the newly added nitrogen (N) peak were the characteristic peaks for ITO/ZnO/fullerene derivatives. The XPS spectra indicated that the two fullerene derivative layers were obtained successfully. Figure 5c shows the normalized C 1s intensity of the three different samples, which indicated that the binding energy of main peaks of the two fullerene derivatives were smaller than ITO/ZnO (about 285 eV), and the intensity of the peak located at 288.6 eV also decreased obviously with modification by fullerene derivatives. The author thought the difference of C 1s spectra between the three samples was ascribed to the fullerene derivative layer. Covered by the fullerene derivative layer, the surface properties of ZnO can be improved and the trap sites can also be decreased effectively. The comparison of atomic concentrations between O 1s, C 1s, and Zn 2p are shown in Figure 5d. By touching the ZnO surface with its hydrophilic block, the fullerene block ordered toward the outside direction and led to more carbon and less oxygen results. With C60-2DPE and C60-4HTPB formed in a uniform film and sharp shape on ZnO, respectively, most ZnO was covered by fullerene derivatives, which also led to the decrease of Zn 2p of the two modified samples.

2.5. Ultraviolet Photoelectron Spectroscopy. For the three samples, Figure 6 presented their ultraviolet photoelectron spectroscopy (UPS) spectra, UV−vis absorption spectra, transmittance spectra, and their energy. As presented in Figure 6a, the highest occupied molecular orbital (HOMO) value was obtained based on eq 1 (where $\hbar \nu$ was 21.2 eV, and $E_{\text{cutoff}}$ and $E_{\text{onset}}^\text{HOMO}$ were obtained from UPS spectra).

$$E_{\text{HOMO}} = \hbar \nu - (E_{\text{onset}}^\text{HOMO} - E_{\text{cutoff}})$$

As summarized in Table 1, the HOMO level energy of ITO/ZnO, ITO/ZnO/C60-2DPE, and ITO/ZnO/C60-4HTPB were −7.75, −6.94, and −7.10 eV, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of −4.65 eV for ITO/ZnO, −3.94 eV for ITO/ZnO/C60-2DPE, and −4.08 eV for ITO/ZnO/C60-4HTPB were obtained from their HOMO values and band gaps. A band gap of 3.00 and 3.02 eV for the two fullerene derivatives was obtained from their UV−vis absorption spectra (Figure 6b). In Figure 6c, all three different samples showed high transmittance in the range of 400−800 nm, while the decreased transmittance of the samples with the modification layer may be caused by the added ultrathin layer. The energy level diagrams of the three samples are shown in Figure 6d. The transmittance spectra for two different samples are also shown in Figure 6e.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Spectra of ZnO and ZnO/fullerene derivatives: (a) UPS spectra, (b) UV−vis absorption spectra, (c) transmittance spectra, and (d) energy level diagrams.

| samples       | $E_{\text{LUMO}}$ ($) | $E_{\text{HOMO}}$ (UPS) | $E_{\text{cutoff}}$ ($E_{\text{onset}}^\text{HOMO}$) |
|---------------|------------------------|--------------------------|-----------------------------------------------|
| ITO/ZnO      | 3.10                   | −7.75                    | −4.65                                          |
| ITO/ZnO/C60-2DPE | 3.00                  | −6.94                    | −3.94                                          |
| ITO/ZnO/C60-4HTPB | 3.02                  | −7.10                    | −4.08                                          |
samples are shown in Figure 6d, and they demonstrated that the introduction of fullerene derivatives could reduce the work function of ZnO effectively.

2.6. Application in OSCs. Because of the amphipathic characteristics of C_{60}-4HTPB and C_{60}-2DPE, two novel materials were employed as the cathode buffer layer (CBL) in the inverted OSC device and the device with structure of ITO/ZnO/fullerene derivatives/PTB7-Th:PC_{71}BM/MoO_{3}/Al. The related curves are displayed in Figure 7, and the corresponding data are summarized in Table 2. For TA devices, the average PCE of the devices boosted sharply from 8.13% for bare ZnO to 8.86% for ZnO/C_{60}-2DPE and 9.21% for ZnO/C_{60}-4HTPB. The J–V curves of the TA devices are shown in Figure 7a. The current density (J_{sc}) was enhanced from 16.71 to 17.94 and 18.67 mA/cm^{2} for the C_{60}-2DPE- and C_{60}-4HTPB-based devices, respectively. The dark current densities of devices with TA C_{60}-2DPE and C_{60}-4HTPB layers were smaller than those with bare ZnO (shown in Figure 7c), which demonstrated that the introduced fullerene derivative layer could inhibit the leakage current of the device. The external quantum efficiency (EQE) curves of the TA devices based on ZnO, ZnO/C_{60}-2DPE, and ZnO/C_{60}-4HTPB are given in Figure 7e. Evidently, the devices based on C_{60}-2DPE and C_{60}-4HTPB ETLs displayed better EQE values than those based on bare ZnO. For SA devices, the PCEs of C_{60}-2DPE- and C_{60}-4HTPB-modified devices were as high as 8.75 and 8.61%, respectively. The enhancement of efficiencies should also be ascribed to J_{sc}, which were 17.53 and 17.51 mA/cm^{2} for SA C_{60}-2DPE- and C_{60}-4HTPB-based devices, respectively, as presented in Figure 7b. The curves shown in Figure 7d also demonstrated that the fullerene derivative layer could inhibit leakage current of the device. The EQE curves of devices based on C_{60}-4HTPB and C_{60}-2DPE also showed better EQE values than those based on ZnO (as presented in Figure 7f).

Compared with the device parameters of TA and SA devices based on different CBLs, it was found that the treatment of toluene failed to get higher PCE for OSC devices. The novel material C_{60}-2DPE was a better choice to modify ZnO in inverted OSCs than in C_{60}-4HTPB, and this result of devices also matched with the UPS measurement. It was inferred that the amine group of C_{60}-2DPE preferred to form a hydrogen bond with ZnO, which was greatly effective in decreasing the

Table 2. Device Parameters of OSCs Based on Different CBLs

| CBLs          | annealing | V_{oc} (V) | J_{sc} (mA/cm^{2}) | FF (%) | PCE (%) |
|---------------|-----------|------------|--------------------|--------|---------|
| ZnO           | 0.78 ± 0.005 | 16.71 ± 0.02 | 62.47 ± 0.08 | 8.13 ± 0.11 |
| ZnO/C_{60}-2DPE | TA        | 0.80 ± 0.008 | 17.94 ± 0.08 | 63.82 ± 0.20 | 9.21 ± 0.10 |
| ZnO/C_{60}-2DPE | SA        | 0.79 ± 0.006 | 17.53 ± 0.06 | 63.21 ± 0.15 | 8.75 ± 0.13 |
| ZnO/C_{60}-4HTPB | TA       | 0.79 ± 0.007 | 18.67 ± 0.10 | 60.05 ± 0.23 | 8.86 ± 0.08 |
| ZnO/C_{60}-4HTPB | SA       | 0.79 ± 0.006 | 17.51 ± 0.06 | 61.74 ± 0.18 | 8.61 ± 0.07 |

Figure 7. (a) J–V characteristics of TA devices, (b) J–V characteristics of SA devices, (c) dark current of TA devices, (d) dark current of SA devices, (e) EQE curves of TA devices, and (f) EQE curves of SA devices.
energy level of ZnO. The ammonium salt group of C_{60}-4HTPB can also form the interfacial dipole and change the energy level of ZnO. Both the hydrogen bond and interfacial dipole could improve the interface compatibility between the ZnO and active layer, thus leading to more effective electronic transmission.

3. CONCLUSIONS

Two novel-functionalized amphiphilic diblock fullerene derivatives C_{60}-2DPE and C_{60}-4HTPB were synthesized and applied as the modified layer on ZnO in OSC devices. Based on their amphiphatic characteristics, the solvent treatment was introduced to cause self-assembly of the two materials and tested by XRD spectra. When used as the interface modification material, C_{60}-2DPE and C_{60}-4HTPB formed different shapes on the surface of ZnO. The functionalized fullerene derivatives can also decrease the energy level of ZnO and enhance the interface compatibility between the ZnO and active layer, which could realize efficient electron transfer from the active layer to the electrode. Device efficiencies of 9.21 and 8.86% based on the PTB7-Th:C_{61}BM system were obtained with introduction of C_{60}-2DPE and C_{60}-4HTPB without treatment of toluene, respectively, with an enhancement of 13 and 9% compared with the control device. However, all devices with SA ZnO/fullerene derivative CBLs of C_{60}-2DPE and C_{60}-4HTPB showed lower PCE than the devices with TA CBLs. The results demonstrated that the solvent treatment may cause a negative effect on the two fullerene derivatives when they were used as the modification layer on ZnO in inverted OSCs. Comparing the synthesis line, solubility, morphological distribution on ZnO, energy level by modifying ZnO, device preparation, and device parameters of TA or SA devices, the author has concluded that the functionalized amphiphilic diblock fullerene derivative C_{60}-2DPE was a better choice to be an interface material modifying ZnO in inverted OSCs than C_{60}-4HTPB, and the TA device could also get better device parameters than the SA device.

4. EXPERIMENTAL METHODS

4.1. Synthesis of Fullerene Derivatives. [6,6]-Phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM) and 1,2-dichlorobenzene (ODCB) were purchased from Luminescence Technology Corp and Aladdin Industrial Corp, respectively. Other reagents and solvents used in this section were all purchased from Sinopharm Chemical Reagent. The synthetic scheme of C_{60}-2DPE and C_{60}-4HTPB is shown in Scheme 1, and the 1H NMR spectra are shown in Figures S2–S9. The most critical step during the synthesis of the two fullerene derivatives was the esterification reaction. In consideration of the great diversity in solubility of the fullerene block and functionalized fluorene block, the esterification reaction was carried out in a mixed solvent of ODCB and N,N-dimethylformamide (DMF) (in the same volume). Finally, the crude product was washed with ODCB and methanol to remove the extra fullerene and hydrophilic-conjugated fluorene block, respectively. The products left were the fullerene derivatives C_{60}-2DPE and C_{60}-4HTPB, respectively, which all had well solubility in DMSO. The three-dimensional (3D) architecture of PC_{61}BA, 2DPE, 4HTPB, C_{60}-2DPE, and C_{60}-4HTPB are shown in Figure S10, which showed the conjugated main chain in conjugated amphiphilic diblock fullerene derivatives obviously.

4.1.1. 1H NMR Spectra

- [6,6]-Phenyl-C_{61}-butyric Acid (PC_{61}BA). PC_{61}BA was synthesized according to the literature.1

4.1.2. 2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (a).

4.1.3. 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-ylphenyl)ethan-1-ol (b).

Scheme 1. Synthetic Scheme of C_{60}-2DPE and C_{60}-4HTPB
4.1.4. 2,2′-(2-Bromo-9-H-fluorene-9,9-diyl)bis(N,N-dimethylthelyan-1-amine) (c). Bromofluorene (5.00 g, 20.4 mmol), 2-dimethylaminomethyl chloride hydrochloride (8.81 g, 61.2 mmol), tetrabutylammonium bromide (0.5 g, 1.55 mmol), and sodium hydride (25 g, 625 mmol) were added into a mixture of DMSO (50 mL) and water (25 mL) under nitrogen. After stirring for 6 h, the solution was poured into water (100 mL) and then washed with ether, brine, and anhydrous magnesium sulfate successively. The pure product (5.67 g, 72%) was obtained with silica gel column chromatography. 

1H NMR (600 MHz, MeOD): δ 1.47 (3H, d, J = 8.60 Hz), 2.28 (3H, d, J = 8.08 Hz), 7.36 (1H, d, J = 3.16 Hz), 7.46 (1H, d, J = 4.92 Hz), 7.49 (1H, d, J = 8.16 Hz), 7.73 (1H, dd, J = 3.52, 4.72 Hz).

4.1.5. 2-(4-(9,9-Bis(2-dimethylamino)ethyl)-9H-fluoren-2-yl)phenylethanol-1-ol (2DPE). 2,2′-(2-Bromo-9-H-fluorene-9,9-diyl)bis(N,N-dimethylthelyan-1-amine) (c) (2.0 g, 5.18 mmol), 2-[(4-(4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane-2-yl)phenyl)-ethanol-1-ol (a) (2.57 g, 10.36 mmol), potassium carbonate (6.9 g, 50 mmol), and tetrakis(triphenylphosphine)-palladium(0) (Pd(PPh3)4) (10 mg) were added into a mixture under nitrogen.

Sodium hydroxide (25 g, 625 mmol) were added into a mixture of 100 mL of distilled water and 50 mL of toluene were injected into the mixture. After vigorous stirring at 80 °C for one night, the mixture was extracted by trichloromethane (CHCl3) (100 mL). The organic layer was washed with brine (100 mL) for three times and then dried by anhydrous sodium sulfate. After removing the solvent, the pure product was obtained with silica gel column chromatography. 

1H NMR (600 MHz, CDCl3): δ 1.16 (1H, d, J = 2.16 Hz), 1.20 (2H, d, J = 6.32 Hz), 2.22 (4H, dd, J = 6.04, 9.76 Hz), 3.11 (4H, t, J = 6.52 Hz), 7.01 (2H, d, J = 8.72 Hz), 7.33 (1H, d, J = 1.44 Hz), 7.36 (2H, d, J = 7.72 Hz), 7.38 (1H, d, J = 1.48 Hz), 7.56 (1H, d, J = 1.36 Hz), 7.59 (2H, d, J = 8.72 Hz), 7.71 (2H, d, J = 7.96 Hz).

4.1.9. 4-(9,9-Bis(3-bromopropyl)-9H-fluoren-2-yl)phenol (f). 9-Bis(3-bromopropyl)-2-(4-methoxyphenyl)-9H-fluorene (e) (1.0 g, 1.95 mmol) was dissolved in dried DCM (20 mL). Borontribromide (0.385 mL, 4.07 mmol) was injected into the mixed solution under nitrogen. After stirring at room temperature overnight, the solvent was removed under reduced pressure, and then the crude product was purified by silica gel column chromatography. The product (0.84 g) was obtained with a yield of 86%. 

1H NMR (600 MHz, CDCl3): δ 1.18 (2H, d, J = 6.96 Hz), 2.20 (1H, d, J = 1.38 Hz), 2.22 (2H, d, J = 2.70 Hz), 2.23 (1H, d, J = 1.62 Hz), 3.11 (4H, t, J = 6.54 Hz), 6.94 (2H, d, J = 8.46 Hz), 7.33 (1H, d, J = 7.32 Hz), 7.37 (1H, d, J = 3.66 Hz), 7.37 (2H, d, J = 18.25 Hz), 7.72 (2H, d, J = 7.56, 11.76 Hz).

4.1.10. 3,3′-(2-(4-Hydroxyphenyl)-9H-fluorene-9,9-diyl)bis(N,N,N-trimethyprop-1-aminium)bromide (4HTPB). 4-(9,9-Bis(3-bromopropyl)-9H-fluoren-2-yl)phenol (f) (0.75 g, 1.50 mmol) was dissolved in dried THF (30 mL). Then, trimethylaminealcoholic solution (6 mL, 10 mmol) was added into the mixture under nitrogen for three times. After stirring at room temperature for 24 h, the solvent was removed under reduced pressure, and the crude product was extracted with DCM and methanol by a soxhlet apparatus. The methanol fraction was retained as the product (0.88 g, 95%) after removing the solvent under vacuum. 1H NMR (600 MHz, MeOD): δ 1.19 (3H, t, J = 17.26 Hz), 1.19 (3H, dd, J = 6.09, 17.92 Hz), 2.28 (4H, dq, J = 5.00, 18.27 Hz), 2.30 (2H, d, J = 16.03 Hz), 3.18 (3H, dd, J = 4.23, 5.55 Hz), 3.20 (2H, d, J = 6.12 Hz), 6.93 (2H, d, J = 4.86 Hz), 6.93 (2H, d, J = 8.58 Hz), 7.44 (1H, d, J = 1.02 Hz), 7.45 (1H, dd, J = 1.17, 5.61 Hz), 7.64 (3H, d, J = 8.70 Hz), 7.68 (1H, dd, J = 1.56, 7.92 Hz), 7.83 (1H, dd, J = 1.14 Hz), 7.87 (1H, d, J = 7.50 Hz), 7.89 (1H, d, J = 7.92 Hz).

4.1.11. [6,6]Phenyl-C51-butycaracid-3,3′-(2-(4-hydroxyphenyl)-9H-fluorene-9,9-diyl)bis(N,N,N-trimethyprop-1-aminium)bromide (C60-4HTPB). PC60BA (100 mg, 0.112 mmol), 4HTPB (80 mg, 0.224 mmol), and 4-dimethylaminopyridine (DMAP) (12 mg, 0.098 mmol) were dissolved in the mixed solvent of ODCB (15 mL) and DMSO (15 mL). Then, the solution of N,N′-dicyclohexylcarbodiimide (DCC) (21 mg, 0.102 mmol) in ODCB (5 mL) was added dropwise to the mixed solution. Stirring at 0 °C for two days and at room temperature for another day, the mixture was centrifuged at high speed in methanol and ODCB, respectively. The obtained insoluble solid was put into dialysis membranes with a molecular weight cutoff of 1000 and then stirred in methanol, ODCB, and DMSO. The DMSO fraction was retained as the product (C60-2DPE) (34 mg, 25%) after removing the solvent.

4.1.7. 2-Bromo-9,9-bis(3-bromopropyl)-9H-fluorene (d). Under nitrogen, bromofluorene (5 g, 20.4 mmol), 1,3-dibromopropane (20.5 g, 101.55 mmol), tetrabutylammonium bromide (0.5 g, 1.55 mmol), and sodium hydride (25 g, 625 mmol) were added into water (25 mL). After reaction at 75 °C for 15 min, the solution was transferred into a separatory funnel and washed with DCM, brine, and anhydrous magnesium sulfate successively. The pure product (3.70 g, 37.5%) was obtained with silica gel column chromatography.

1H NMR (600 MHz, CDCl3): δ 1.13 (2H, d, J = 2.64 Hz), 1.13 (4H, t, J = 14.68 Hz), 1.14 (2H, d, J = 4.80 Hz), 2.14 (3H, d, J = 7.02 Hz), 2.14 (3H, d, J = 8.04 Hz), 3.13 (4H, t, J = 6.57 Hz), 7.43 (1H, t, J = 19.21 Hz), 7.49 (4H, d, J = 1.80 Hz), 7.49 (4H, d, J = 8.46 Hz), 7.51 (4H, d, J = 17.89 Hz), 7.51 (2H, d, J = 8.40 Hz), 7.53 (2H, d, J = 1.02 Hz).
temperature for another day, the mixture was centrifuged at high speed in water and ODCB. The obtained insoluble solid was put into dialysis membranes with a molecular weight cutoff of 1000 and then into water, methanol, ODCB, and DMSO. The DMSO fraction was kept as the product (C_{60}-2DPE) (25 mg, 15%) after removing the solvent.

### 4.2. Preparation of Films.

The solvent 2-methoxyethanol (15 mL) by dissolving zinc acetate dihydrate (Zn(CH\(_2\)COO)\(_2\)) and 2H\(_2\)O, 99.9%, 0.98 g) was stirred at 70 °C for 1 h, and then 2-aminoethanol (NH\(_2\)CH\(_2\)CH\(_2\)OH, 99.5%, 275 μL) was injected into the above solution and then stirred at 70 °C for another 2 h. Finally, the solution was allowed to cool down to room temperature and stirred overnight. With ultrasonication in detergent, deionized water, acetonitrile, and isopropyl sequentially, the ITO substrate dried in an oven at 80 °C overnight. The ZnO layer was formed on the ITO substrate by spin-coating with a speed of 4000 rpm and annealing at 220°C for another 2 h. The ZnO layer was then annealed at 250°C for 1 h, and then, 2-methoxyethanol (2-methoxyethanol, 99%, 275 μL) was injected into the above solution and then stirred at 70 °C for another 2 h. Finally, the solution was allowed to cool down to room temperature and stirred overnight. With ultrasonication in detergent, deionized water, acetonitrile, and isopropyl sequentially, the ITO substrate dried in an oven at 80 °C overnight. The ZnO layer was formed on the ITO substrate by spin-coating with a speed of 4000 rpm and annealing at 220°C for another 2 h.

4.3. Preparation of the Inverted OSC Device.

The mixed compound of PTB7-Th:PC\(_{71}\)BM (10 mg: 15 mg) was dissolved in a solution of 0.97 mL dichlorobenzene and 0.03 mL 1,8-diodooctacene. The active layer was formed on three different CBLs by spin-coating the cooled mixture solution after stirring at 60 °C for 1 h with a speed of 1500 rpm for 60 s. Then, the MoO\(_3\) and top Al layer with a thickness of 6 and 100 nm, respectively, were thermally deposited in vacuum onto the active layer at a pressure of ca. 3.0 × 10\(^{-5}\) Pa after the active layer was placed inverted in a glovebox for 1 h.

### 4.4. Instrument.

For the two functionalized amphiphilic diblock fullerene derivatives, their absorption spectra and \(^1H\) NMR spectra were measured with an ultraviolet spectrometer UV-3600 and Bruker AscendTM 600 MHZ. The surface hydrophilicity of ITO/ZnO/fullerene derivatives samples were measured with a contact angle meter and Keithley 485 picoammeter. The authors declare no competing financial interest.

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