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Electrostatic Self-Assembly Conjugated Polyelectrolyte-Surfactant Complex as an Interlayer for High Performance Polymer Solar Cells

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A simple method is demonstrated to improve the film-forming properties and air stability of a conjugated polyelectrolyte (CPE) without complicated synthesis of new chemical structures. An anionic surfactant, sodium dodecybenzenesulfonate (SDS), is mixed with cationic CPEs. The electrostatic attraction between these two oppositely-charged materials provides the driving force to form a stable CPE-surfactant complex. Compared with a pure CPE, this electrostatic complex is not only compatible with highly hydrophobic bulk-heterojunction (BHJ) films, e.g. poly(3-hexylthiophene):[6,6]-phenyl C_{61} butyric acid methyl ester (P3HT:PCBM), but also works well with other low bandgap polymer-based BHJ films. Using this complex as a cathode interface layer, a high power conversion efficiency of 4% can be obtained in P3HT:PCBM solar cells together with improved stability in air. Moreover, ~20% performance enhancement can also be achieved when the complex is used as an interlayer to replace calcium metal for low bandgap polymer-based BHJ systems.

1. Introduction

Over the past few years, extensive research has been conducted on developing bulk-heterojunction (BHJ) polymer solar cells (PSCs).[1] High performance devices always rely on both photoactive materials innovation and device optimization. In the last three years, some high performance BHJ material systems have been developed, providing power-conversion-efficiency (PCE) of >7%.[2] Further improvement can be expected with device optimization, including film morphology control,[3] optical modulation,[4] and interface modification.[5] Interface modification is commonly used to improve device performance. Solution-processable interface materials, such as metal oxides,[6] salts,[7] fullerene derivatives,[8] polymers,[9] and self-assembled monolayers,[10] have been utilized for interface modification in PSCs.

Recently, conjugated polyelectrolytes (CPEs) have emerged as a novel n-type interlayer.[11] CPEs are often soluble in alcohol/water-based polar solvents, which ensure their direct deposition on top of the active layer without damaging underlying films.[11,12] The CPE layer is believed to form dipoles at the organic/metal interface and facilitate efficient electron transport.[11l–11o] Most importantly, CPEs can be synthesized with various structures.[11h,11p] This provides the flexibility to tune their properties so that CPEs will be compatible with different active layers. For example, Bazan et al. have used a polythiophene-fluorene-based CPE in PSCs.[11n] Over 20% efficiency improvement was achieved with a CPE interface compared with that using an Al-only electrode. Wu et al. have also incorporated a polyfluorene-based CPE into thieno[3,4-b]-thiophene/benzodithiophene copolymer (PTB7)-based PSCs. Significant improvements of photovoltaic properties such as open-circuit voltage (V_{oc}), short circuit current (J_{sc}), and fill factor (*FF*) were achieved resulting in the PCE of >8%.[11o]

As the most popular electron donor material, poly(3-hexylthiophene) (P3HT) can be blended with [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) to form a P3HT:PCBM BHJ film.[13] The P3HT:PCBM film surface is highly hydrophobic. The inherent incompatibility between the polar CPEs and P3HT:PCBM films results in poor CPE film-formation. As a result, the series resistance will be greatly increased leading to poor charge collection.[14] This obviously limits the application of CPEs. For example, in our preliminary experiments, a cationic CPE, poly[3-(6-trimethylammoniumhexyl)thiophene] (PTMAHT, **Figure 1**A), was used as cathode interface layer in P3HT:PCBM-based devices. The optimal device only showed a PCE of 2.55%, with a V_{oc} of 0.56 V, a J_{sc} of 7.95 mA·cm^{-2}, and a *FF* of 57.2% (Figure S1 and Table S1). Contact angle and optical microscope measurements (Figure S2) indicated that the PTMAHT/methanol solution has poor wettability on the highly hydrophobic P3HT:PCBM surface, resulting in discontinuous PTMAHT film coverage. To improve the compatibility between the CPE and varied active layer materials, chemical structure tuning provides an effective approach.[11h,11p] For example, Kim et al. have demonstrated a polyfluorene-based CPE containing oligo(ethylene oxide) side chains, which can improve the compatibility between CPE and P3HT:PCBM films.[15]

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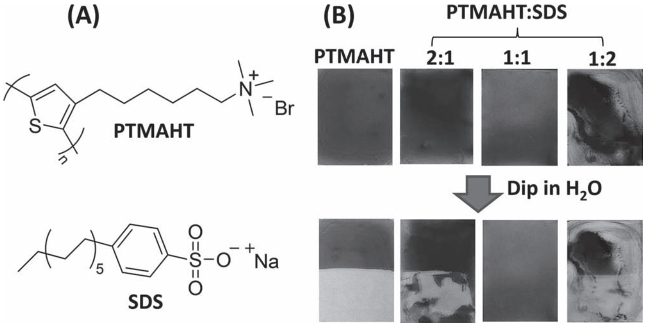

Figure 1. (A) Chemical structure of cationic PTMAHT and anionic SDS. (B) Photographs of the films containing PTMAHT and SDS with different molar ratios. The films were then dipped into water to test their solubility. Sample size: 1.5 cm × 2.2 cm.

In this work, we demonstrate a simple method of tuning the properties of CPEs without complicated synthesis of new chemical structures. An anionic surfactant is mixed with the cationic PTMAHT. The electrostatic attraction between these two oppositely-charged materials provides the driving force to form a stable CPE-surfactant complex.[16] Compared with the pure CPE, the electrostatic complex is not only compatible with highly hydrophobic P3HT:PCBM films, but also works well with some less hydrophobic BHJ films, like those based on PTB7.[17] By using the complex as an interface layer, a high efficiency of >4% can be achieved in a P3HT:PCBM device together with improved device stability in air.

2. Results and Discussion

PTMAHT has been used before as a cationic CPE material as reported in literatures.[11n,14] The anionic surfactant sodium dodecylbenzenesulfonate (SDS, Figure 1A) is used as the counterpart to mix with the cationic PTMAHT at a molar ratio of 1:1 (PTMAHT:SDS). Although both PTMAHT and SDS are water-soluble materials on their own, as soon as stoichiometric amounts of PTMAHT and SDS were mixed in water, a deep-red precipitate formed. This is ascribed to the electrostatic attraction between the cationic moieties in PTMAHT and anionic moieties in SDS, resulting in polymer backbones surrounded by nonpolar alkyl side chains. The precipitates were then collected, washed with de-ionized water to remove the residual water-soluble compounds and salts and finally dried in vacuum to yield the stoichiometric PTMAHT:SDS complex.

It was also found that the blend ratio affects the properties of the resulting complexes. Figure 1B compares the solubility of the films prepared with different PTMAHT:SDS molar ratios. The bottom parts of the films were dipped into water to check their solubility in water. The PTMAHT-only film was completely dissolved by water. In contrast, water did not affect the stoichiometric PTMAHT:SDS complex film, even when the entire film was immersed in water over a couple weeks. This simple experiment shows the stability of the complex against humidity, which can potentially improve stability when used in devices. In contrast, the PTMAHT:SDS films with the non-stoichiometric blend ratios (2:1 and 1:2) were destroyed by water. For the 2:1 ratio, the extra water-soluble PTMAHT side chains can still retain its good solubility in water. However, for the 1:2 ratio with extra SDS counter ions, "mixed micelles" are most likely to form with hydrophilic shells, leading to its good solubility in water.[16a–16c]

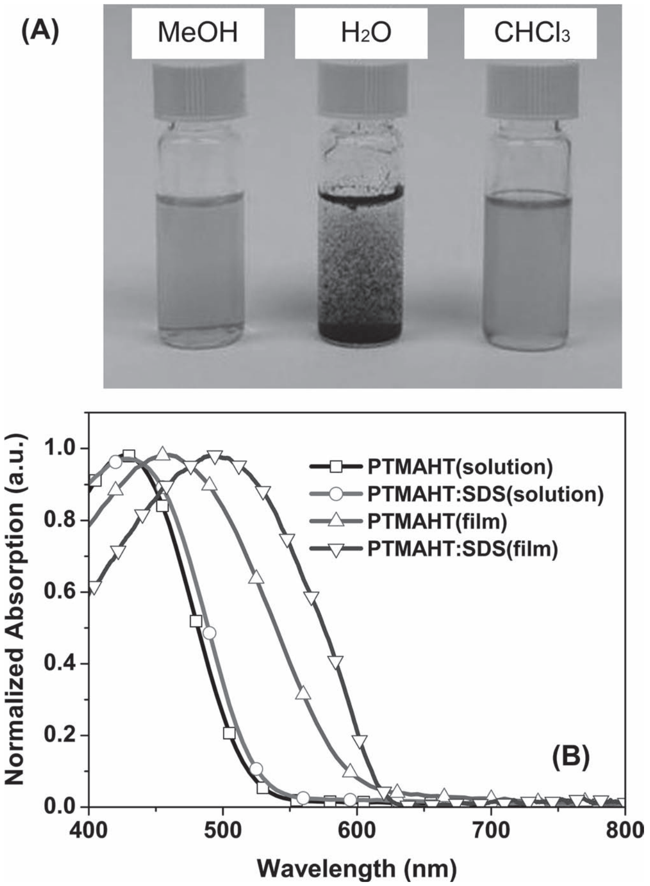

Figure 2. (A) Photographs of the solutions of stoichiometric PTMAHT:SDS complex in different solvents at a concentration of 10 mg/mL. (B) UV-visible absorption spectra of PTMAHT and PTMAHT:SDS in solution or film states.

Figure 2A demonstrates the solubility of the PTMAHT:SDS complex in different solvents. The complex has good solubility in both methanol and chloroform, but is insoluble in water. Figure 2B compares the UV-vis absorption spectra of both PTMAHT and PTMAHT:SDS complex. In the solution state, both PTMAHT and PTMAHT:SDS have similar absorption spectra, with their absorption onset wavelengths (λ_{onset}) at ~520 nm. This indicated that the electrostatic interaction between PTMAHT and SDS doesn't affect the optical properties of the PTMAHT main chains, which are freely dispersed in solution. However, in the film state, a different phenomenon was observed. The λ_{onset} of pristine PTMAHT film is ~593 nm (2.10 eV), which is about 70 nm red-shifted as compared to that in the solution. This red-shift is ascribed to the increased effective range of π-electron delocalization due to the π–π packing of polymer chains in solid film, relative to the freely stretched molecular chains in solution state.[18] After attaching the SDS units onto PTMAHT, the stoichiometric complex give a λ_{onset} at

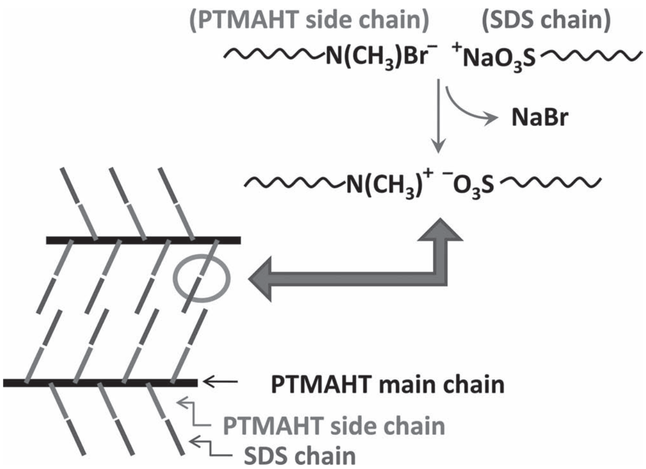

Figure 3. Schematics of the electrostatic attraction to form the self-assembled stoichiometric PTMAHT:SDS complex.

615 nm in the film state, which is another ~20 nm redshifted compared with that of PTMAHT film. This indicates that the introduction of SDS side chain into PTMAHT will further change the conformation of PTMAHT backbone, resulting in much more ordered packing of polymer backbones,[19] as illustrated in **Figure 3**.

Due to its hydrophobic alkyl side chains, the PTMAHT:SDS complex can be easily coated onto the highly hydrophobic P3HT:PCBM surface from its methanol solution. No obvious pinholes were observed after PTMAHT:SDS coating (Figure S3A), indicating the formation of a uniform film. Contact angle measurements (Figure S3B) also showed that the hydrophobic P3HT:PCBM film surface was covered by a thin PTMAHT:SDS film, resulting in the contact angle change from 105° (Figure S2) to 70.6° (Figure S3b).

Because of its superior coating properties, the PTMAHT:SDS complex was employed as a cathode interface modification layer (or interlayer) in P3HT:PCBM-based BHJ polymer solar cells. PTMAHT:SDS was spincoated onto P3HT:PCBM BHJ film from its methanol solution (0.125 wt%) at 5000 rpm to form a ~5 nm interlayer. The device structure is ITO/PEDOT:PSS/P3HT:PCBM/interlayer/Al. Different interlayers were also employed for comparison. **Figure 4** shows the plotted current density (*J*) vs. voltage (*V*) curves for the devices measured under AM 1.5G solar irradiation at an intensity of 100 mW·cm^{-2}. **Table 1** summarizes the device performance. The interlayer-free device (Al-only cathode) exhibited poor device performance with a V_{oc}, J_{sc}, *FF*, and *PCE* of 0.48 V, 7.97 mA·cm^{-2}, 55.3%, and 2.12%, respectively. In the standard Ca/Al-based control device, a typical V_{oc} of 0.60 V, J_{sc} of 9.14 mA·cm^{-2}, and *FF* of 69.4% could be achieved, giving a *PCE* of 3.83%. By replacing the evaporated Ca with solution-processed PTMAHT:SDS complex, a higher PCE of 4.01% can be achieved with a V_{oc} of 0.62 V, a J_{sc} of 9.54 mA·cm^{-2}, and a *FF* of 67.8%. As a comparison, pure anionic surfactant SDS was also used to modify the cathode interface, however, the device only gave a PCE of 2.63%, with a V_{oc} of 0.53 V, a J_{sc} of 8.45 mA•cm^{-2}, a *FF* of 58.8%. These results show the superior interface modification properties of the stoichiometric PTMAHT:SDS complex. The improved film-forming capability of PTMAHT:SDS complexes on the BHJ layer results in the high device efficiency.

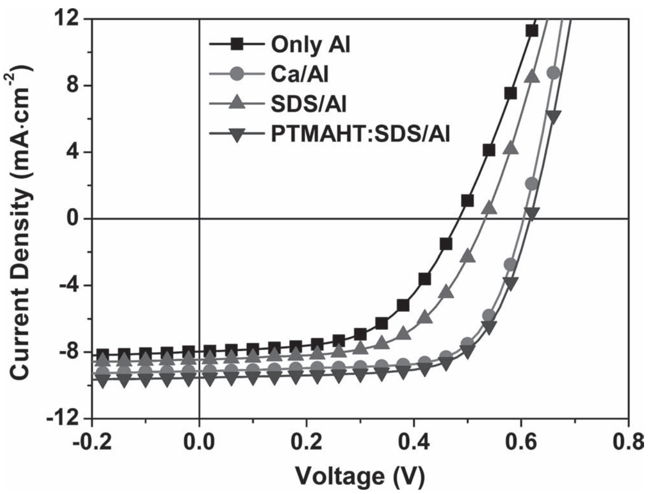

Figure 4. *J*–*V* Characteristics of ITO/PEDOT:PSS/P3HT:PCBM/interlayer/Al devices with different interlayer materials.

Beyond the device efficiency improvement, enhanced device stability was also observed when using PTMAHT:SDS complex as the cathode interlayer. **Figure 5** compares the air stability test of devices with different interlayers. Devices *without encapsulations* were placed in air (humidity: ~55%; Temperature: ~24 °C) in the dark for various times before measurements. Ca/Al is the most popular cathode for PSC devices. For the device using Ca/Al electrode, although high device performance can be simply achieved, the device shows poor stability in air due to the high reactivity of Ca with oxygen and moisture. PCE will decrease by ~50% after ~5 h exposure in air. Although CPEs are good alternative interlayer for high device performance, the water-soluble side groups may also be sensitive to moisture, which will result in the rapid degradation of devices. For example, the device using PTMAHT as cathode interlayer shows serious degradation, which is even faster than Ca/Al-based device. In contrast, the device using PTMAHT:SDS complex as cathode interlayer shows significantly improved stability. Both V_{oc} and *FF* remained almost unchanged during the air exposure test. PCE can still maintain about 80% of the initial value after 12 h exposure in air, indicating its superior air stability. These results also suggest that the electrostatic complexion between CPE and surfactant provides an effective method to stabilize CPE materials, which is promising to achieve a moisture/water-resistant CPE material.[16d,16e]

Table 1. Summary of the photovoltaic parameters of the P3HT:PCBM solar cells fabricated with different interlayer/electrode combinations.

Electrode	V_{oc} *(V)*	J_{sc} *(mA·cm^{-2})*	*FF (%)*	*PCE (%)*
Al	0.48	7.97	55.3	2.12
Ca/Al	0.60	9.14	69.4	3.81
SDS/Al	0.53	8.45	58.8	2.63
PTMAHT:SDS/Al	**0.62**	**9.54**	**67.8**	**4.01**

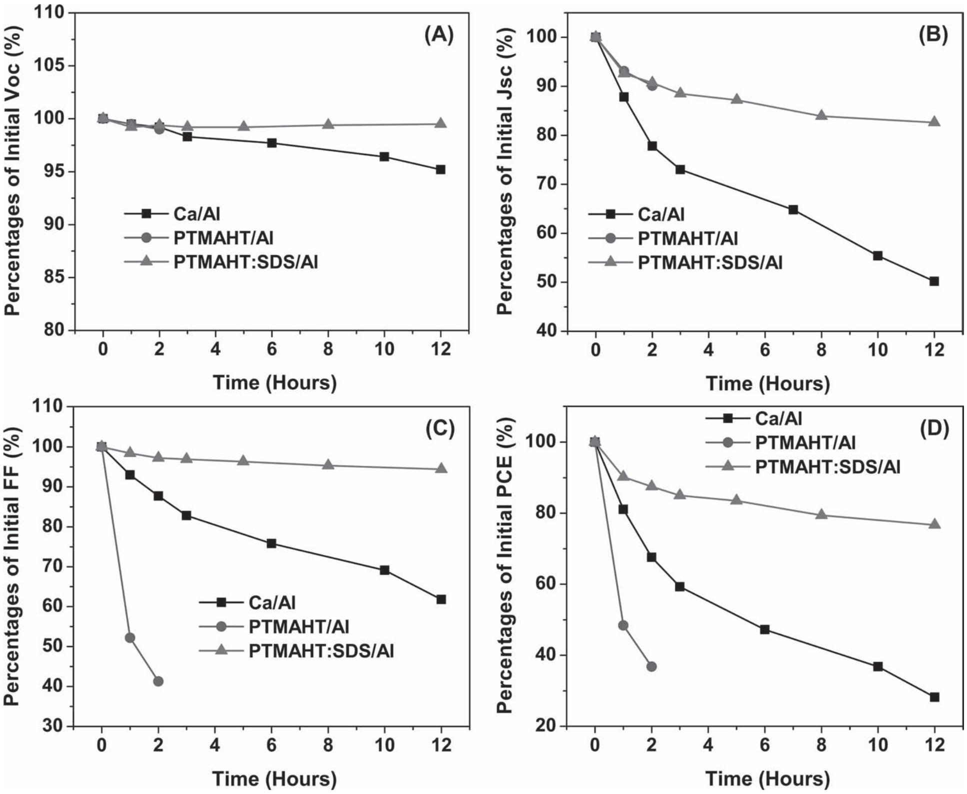

Figure 5. The air-stability test of the unencapsulated devices based on Ca/Al electrode (■), PTMAHT/Al electrode (●) and PTMAHT:SDS/Al electrode (▲). (A) V_{oc}; (B) J_{sc}; (C) *FF*; (D) *PCE*.

The PTMAHT:SDS complex was also employed in devices composed of a PTB7: [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) BHJ layer[11o,17] and a comparative experimental study was performed. The device performance is shown in Figure S4 and Table S2. The devices with an Al-only cathode exhibited a V_{oc}, J_{sc}, *FF*, and *PCE* of 0.68 V, 11.2 mA·cm^{-2}, 60.0%, and 4.57%, respectively. The devices with a Ca/Al cathode showed improved photovoltaic characteristics, with a V_{oc} of 0.72 V, a J_{sc} of 11.9 mA·cm^{-2}, a *FF* of 63.7%, and a *PCE* of 5.46%. When PTMATH:SDS was used as cathode interlayer, the device demonstrated an improved V_{oc} of 0.77 V, J_{sc} of 12.3 mA·cm^{-2}, *FF* of 68.3%, and *PCE* of 6.47%. These improvements are consistent with the results demonstrated in a recent publication using PFN interlayers.[11o] This implies that the CPE:surfactanct complex is not only compatible with the P3HT:PCBM, but also works very well with other BHJ film, indicating its wide compatibility with different BHJ films. However, the best performance here is not as high as the reported results due to the limitation of PTB7 material quality in current batch.[11o]

3. Conclusions

In summary, we have demonstrated a simple method to prepare a high performance conjugated polyelectrolyte interlayer for polymer solar cells. Electrostatic attraction between two oppositely-charged materials is utilized to tune the properties of conjugated polyelectrolyte. This is obviously much easier compared with the structure tuning by complicated chemical synthesis. As an example, we have chosen the anionic surfactant SDS to modify the cationic PTMAHT polyelectrolyte, resulting in the PTMAHT:SDS complex. Such a CPE:surfactant complex possesses improved film-forming properties on the highly hydrophobic P3HT:PCBM film surface. Above 4% PCE can be achieved when use PTMAHT:SDS complex as cathode interlayer for P3HT:PCBM-based devices. In addition, the PTMAHT:SDS complex interlayer can improve the device stability in air. Moreover, the complex is also compatible with other PSC materials. ~20% improvement in device performance can be achieved for PTB7-based devices.

4. Experimental Section

Synthesis of poly[3-(6-trimethylammoniumhexyl)thiophene] (PTMAHT): The conjugated polyelectrolyte, PTMAHT, was synthesized by modifying the previously reported procedures.[20] The neutral precursor, regioregular poly(3-(6-bromohexyl)thiophene) was synthesized by a Grignard metathesis approach. Then, the cationic PTMAHT was obtained by treating poly(3-(6-bromohexyl)thiophene) with trimethylamine in THF at reflux temperature for 48 h, followed by extraction with water. The water was then removed under reduced pressure. The polymer was dried in vacuum overnight and was obtained as a dark red material.

Preparation of PTMAHT:SDS Complex: PTMAHT and SDS (purchased from Aldrich Co. and used as received) were mixed in water in the 1:1 stoichiometric molar ratio and stirred at room temperature for a couple seconds. The solubility of the complex was reduced in water and it precipitated during this period. Subsequently, the precipitate was collected, and washed three times with de-ionized water by using centrifugation to remove the residual water-soluble PTMAHT, SDS, and salts. Finally, the precipitate was dried under vacuum overnight to yield the purified complex. The molar ratio of PTMAHT to SDS in the complex was verified by the integrated area of resonance peaks at 7.6 ~ 6.9 ppm in the ^{1}H NMR spectrum (400 MHz, dimethylsulfoxide-d_6), corresponding to the protons of in benzene ring (4H, form SDS) and thiophene ring (1H, from PTMAHT). (Figure S5).

Fabrication of Polymer Solar Cells: PCBM and P3HT were purchased from Nano-C and Rieke Metals, respectively. PTB7 sample was obtained from 1-Material Inc. for research test.[11o] Devices were fabricated by spin-coating a layer of PEDOT:PSS (30 nm, Baytron P VP AI 4083) on a pre-cleaned ITO glass, drying at 120°C for 20 min in air, and transferring into a nitrogen-filled glovebox. P3HT (20 mg mL^{-1}) and PCBM (20 mg mL^{-1}) were dissolved in 1 mL of *o*-dichlorobenzene. Then the P3HT:PCBM blend was spin-coated on top of the PEDOT:PSS layer, and solvent annealed at room temperature for 30 min, and then thermally annealed at 150 °C for 10 min. Then a 0.125 wt% PTMAHT:SDS complex/methanol solution was spin-coated on top of the P3HT:PCBM layer in an air atmosphere and baked at 120 °C for 5 min to form an interlayer 5 nm thick. For PTB7-based devices, the PTB7 (10 mg mL^{-1}) and PC$_{71}$BM (15 mg mL^{-1}) were dissolved in 1 mL *o*-dichlorobenzene with 3% diiodooctane, and the blend was coated onto the PEDOT:PSS layer to form a BHJ layer. Subsequently, a 0.04 wt% complex in methanol solution was deposited onto the BHJ surface, without any annealing or heating steps. Finally, a 100-nm-thick Al electrode was deposited by thermal evaporation at a pressure of approximately 10^{-6} Torr. The active area of the device defined by the shadow mask was 0.1 cm^2.

Characterization: *J–V* characteristics of photovoltaic devices were taken using a Keithley 2400 source measurement unit under a simulated AM1.5G spectrum with an Oriel 91191 solar simulator. Absorption spectra were taken using a Hitachi ultraviolet–visible spectrophotometer (U-4100). The NMR spectrum was recorded using a BRUKER ARX-400 FT-NMR spectrometer. The thickness of each layer was determined by a Dektak 150.

Supporting Information

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

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