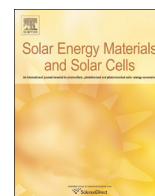




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Application of a water-soluble metallophthalocyanine derivative as a cathode interlayer for the polymer solar cells



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ABSTRACT

A water-soluble metallophthalocyanine (MPc) derivative, 2,3,9,10,16,17,23,24-octakis(2-trimethylaminoethylsulfanyl) zincphthalocyanine octaiodide ($\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$) was synthesized and applied in polymer solar cells (PSCs). A power conversion efficiency (PCE) of 7.06% has been obtained when the $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ was utilized as a cathode interlayer in the PSCs based on a blend of PCDTBT (poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]) and PC₇₁BM ([6,6]-phenyl C₇₁ butyric acid methyl ester) as an active layer. Ultraviolet photoemission spectroscopic (UPS), atomic force microscopy (AFM), contact angle (θ) and mobility measurements demonstrated that an introduction of $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ between active layer and cathode decreased work function of cathode, increased hole mobility and facilitated a balance of electron and hole transport in the PSCs, resulting in a simultaneous improvement of open-circuit voltage, short-circuit current and fill factor.

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1. Introduction

Polymer solar cells (PSCs) have drawn great attention owing to their key advantages of synthetic variability, light weight, low cost, large-area roll to roll fabrication and the lucrative possibility of integration directly into flexible devices [1–6]. Power conversion efficiency (PCE) of PSCs has been over efficiencies of 9% with good ambient stability for single cell devices [7–9]. In order to improve the PCE of PSCs, significant efforts have been made in terms of new material synthesis [10–12], device structure optimization [13–16] and controlling the morphology of the active layer [17–20]. Moreover, studies on the interface between electrodes and active layers have been devoted to improving device efficiency by decreasing charge collection/extraction barriers and forming ohmic contact between electrode and active layer. Significant improvements of PCE have been realized by placing a cathode interlayer (CIL) between the active layer and the metal electrode. It is worth noting that certain alcohol/water-soluble organic or polymeric electrolytes used as CILs can strongly enhance the PCE of PSCs [21]. Because the alcohol/water solubility of the organic materials can avoid intermixing between the active layer and the interlayer, alcohol/water-soluble organic molecules are promising

CIL materials for all solution processed PSCs. Compared to other cathode interfacial layer materials, advantages of alcohol/water-soluble organic materials are apparent in the PSCs due to their simple, vacuum-free and environment-friendly procedure to form film during the device fabrication and universality for different active layer and different metal cathode [22,23]. So far reported CILs improving the device performance mainly consist of polymers [24–34] and organic small molecules [35–49]. Compared to polymers, organic small molecules are more attractive because of their several intrinsic advantages over the conjugated polymer counterpart in terms of easy purification, monodispersity and well-defined structures without end group contaminants and better batch-to-batch reproducibility. Successful alcohol/water soluble small molecular CIL materials include fullerene derivatives [35–39], perylene diimides [40,41], porphyrin [42], pyridinium salt [43], rhodamine with inner salt [44], quinacridone tethered with sodium sulfonate [45], triphenylamine-ureone core featuring a phosphonate side chain [46], tetra-n-alkyl ammonium bromides [47], and metallophthalocyanine (MPc) derivative [48,49].

As a kind of excellent organic semiconductor materials, MPc and its derivatives have been widely used as organic pigments, which have important roles due to their excellent photophysical, semiconducting and electrochemical properties, as well as their stability. Recent investigations have focused on the applications of MPc-based materials in organic electronic devices such as organic

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photovoltaic devices (OPVs) [50–55] and organic field-effect transistors (OFETs) [56,57]. So far, in most of these studies, the MPc compounds were applied as active layers in organic electronic devices, their application beyond active materials has been very limited. Therefore, exploration of the new applications and functions of MPc in organic electronic devices shows great potential. In this contribution, we report a MPc derivative $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ with eight ammonium salts as terminal groups and its application as a CIL in the PSCs. A power conversion efficiency (PCE) of 7.06% has been obtained when the $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ was utilized as a CIL in the PSCs based on a blend of PCDTBT (poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]) and PC₇₁BM ([6,6]-phenyl C₇₁ butyric acid methyl ester) as an active layer. Ultraviolet photoemission spectroscopic (UPS), atomic force microscopy (AFM), contact angle (θ) and mobility measurements demonstrated that an introduction of $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ between active layer and cathode decreased work function of cathode, increased hole mobility and facilitated a balance of electron and hole transport in the PSCs. As a result, a simultaneous improvement of open-circuit voltage, short-circuit current and fill factor has been achieved compared to the only-Al devices without a CIL.

2. Materials and methods

2.1. Materials

4,5-Dichlorophthalonitrile was purchased from Aldrich Chemical Co. Other starting materials were common commercial grade and used as received. PCDTBT (Lot#YY6092C) was purchased from 1-material Chemscitech Inc. (Canada). PC₇₁BM (Lot#14A0021E1) was purchased from American Dye Source (USA).

2.2. Characterization

¹H NMR spectra were measured on a Varian Mercury 300 MHz spectrometer (USA) with tetramethylsilane as the internal standard. Elemental analyses were performed on a flash EA 1112 spectrometer (Germany). MALDI-TOF mass spectra were recorded on Kratos AXIMA-CFR Kompact MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix. Current density–voltage (*J*–*V*) characteristics of the devices were measured under N₂ atmosphere in the glove box by using a Keithley 2400 under illumination and in the dark. Solar cell performance was tested under 1 sun, AM 1.5G full spectrum solar simulator (Photo Emission Tech. Inc., model #SS50AAA–GB) with an irradiation intensity of 100 mW cm^{−2} calibrated with a standard silicon photovoltaic traced to the National institute of metrology, China. External quantum efficiency (EQE) spectra were measured using Q Test Station 2000 (Crowntech Inc. USA) at room temperature in air. In addition, the static contact angles of the as-prepared surfaces were measured with a commercial contact angle system (DataPhysics, OCA 20) at ambient temperature using a 4 μl water droplet as the indicator. AFM images were measured with an S II Nanonavi probe station 300 HV (Seiko, Japan) in contact mode.

2.3. Device fabrication

Fabrication of polymer solar cells, electron-only and hole-only devices: the blend ratio of PCDTBT:PC₇₁BM is 1:4 by weight and the active layer (35 mg mL^{−1}) was spin-cast from a mixed solvent of chlorobenzene/*o*-dichlorobenzene (ratio 1:3). $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ was dissolved in water under the presence of 0.6% acetic acid, the optimal concentration of $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$

solution is found to be 1 mg mL^{−1}. First, the ITO glass substrates were pre-cleaned carefully and treated with plasma for 7 min. PEDOT:PSS (Baytron PVP Al 4083) was spin-coated onto a cleaned ITO and annealed in air at 120 °C for 10 min. Second, blend films of PCDTBT:PC₇₁BM were spin-coated onto the PEDOT:PSS layer and then annealed in a glove box at 75 °C for 10 min, ~5 nm $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ (the thickness was estimated by the attenuation of Au 4f core-level signal of Au substrates in the XPS measurement) was deposited on the active layer by spin-coating; next 100 nm Al was evaporated as a cathode. The active area of each device was 2.0 × 2.0 mm². For the electron-only and hole-only devices, their device structures were: ITO/Al/PCDTBT:PC₇₁BM/ with or without CIL/Al and ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/ with or without CIL/MoOx/Al, respectively.

2.4. Synthesis

The synthesis procedure of 2,3,9,10,16,17,23,24-octakis(2-trimethylaminoethylsulfanyl) zincylphthalocyanine octaiodine $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ is illustrated in Scheme 1. 1,2-Bis-(dimethylaminoethylsulfanyl)-4,5-dicyanobenzene was prepared by a base catalyzed nucleophilic aromatic displacement of 4,5-dichlorophthalonitrile. And then cyclization reaction was employed to afford 2,3,9,10,16,17,23,24-octakis(2-dimethylaminoethylsulfanyl) zincylphthalocyanine ($\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2\text{I}]_8$). Compound $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$ was obtained by methylation of compound $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2\text{I}]_8$ in chloroform in good yields. All new compounds were fully characterized by NMR, elemental analysis or MS.

1,2-Bis-(dimethylaminoethylsulfanyl)-4,5-dicyanobenzene ([S(CH₂)₂N(CH₃)₂]₂PN): 4,5-dichlorophthalonitrile (2.0 g, 10.0 mmol), 2-(dimethylamino) ethanethiol hydrochloride (3.5 g, 25.0 mmol) and K₂CO₃ (8.3 g, 60.0 mmol) were dissolved in 100 mL dry DMSO under nitrogen atmosphere and the mixture was heated at 50 °C for 24 h. After cooling to room temperature, the mixture was then poured into ice water (300 mL) to give a brown solid, which was collected by filtration and washed with water. The crude product was purified by recrystallization from diethyl ether. The brown solid formed was collected by filtration and dried in vacuo, while the etherate filtrate was evaporated and subject to column chromatography using dichloromethane and methanol as eluent giving the brown solid. Yield: 1.9 g (56%). ¹H NMR (300 MHz, CDCl₃): δ 7.50 (s, 2H), 3.16–3.11 (t, *J* = 6.9 Hz, 4H), 2.67–2.65 (t, *J* = 6.9 Hz, 4H), 2.31 (s, 12H). MS (MALDI-TOF): *m/z*: 335.43 [M+H]⁺. Elemental analysis calcd: C 57.45%, H 6.63%, N 16.75%, S 19.17%; found: C 57.32%, H 6.78%, N 16.57%, S 19.18.

2,3,9,10,16,17,23,24-Octakis(2-dimethylaminoethylsulfanyl) zincylphthalocyanine ($\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2\text{I}]_8$): [S(CH₂)₂N(CH₃)₂]₂PN (780.4 mg, 2.0 mmol), zinc acetate (550.0 mg, 3 mmol) and 1,8-diazabicyclo (5.4.0) undec-7-ene (DBU) (304.0 mg, 2.0 mmol) were dissolved in 15 mL *n*-pentanol. Under nitrogen atmosphere, the solution was stirred and heated to reflux for 25 h. After cooling to room temperature, solvent was removed by vacuum evaporation and the crude product was purified by column chromatography using silica gel with dichloromethane and methanol as the eluents to obtain the green powder. Yield: 140.0 mg (17%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.19 (s, 8H), 3.72 (br, 16H), 3.15 (br, 16H), 2.65 (br, 48H). MS (MALDI-TOF): *m/z*: 1401.55 [M+H]⁺. Elemental analysis calcd: C 54.78%, H 6.32%, N 15.97%, S 18.28%; found: C 54.68%, H 6.28%, N 15.99%, S: 18.26%.

2,3,9,10,16,17,23,24-Octakis(2-trimethylaminoethylsulfanyl) zincylphthalocyanine octaiodine ($\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3\text{I}]_8$): A solution of $\text{ZnPc}[\text{S}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2\text{I}]_8$ (200.0 mg, 0.1 mmol) and methyl iodide (425.0 mg, 3.0 mmol) in 30 mL dry chloroform was heated reflux for 10 h. After cooling to room temperature, the green precipitate was filtered off and washed with chloroform. Then the product was dissolved by the acetonitrile-methyl alcohol and dried and

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