

Supporting information for

Solution Processed and Self-assembled Polymerizable Fullerenes/Metal Oxide as an Interlayer for High Efficient Inverted Polymer Solar Cells

Lin Hu¹, Lie Chen^{1,2}, Xiaotian Hu¹, Yiwang Chen^{*1,2}

¹Institute of Polymers/Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China; ²Jiangxi Provincial Key Laboratory of New Energy Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Materials

Malonyl chloride, 10-undecen-1-ol, triethylene glycol monomethyl ether, 1,8-Diazabicyclo[5.4.0]undec-7-ene and Iodine were purchased from Energy Chemical. The C₆₀ was from Nanjing XFNANO Materials Tech Co.,Ltd. All these ingredients were used as received without any further purification. Pyridine, toluene and other chemicals were obtained from Shanghai Reagent Co.,Ltd., and used as received. Regioregular P3HT (Mw = 48300 g/mol, head-to-tail, regioregularity > 90%), [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) (99.5% purity), thieno[3,4-b]thiophene/benzodithiophene(PTB7), [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) and MoO₃ were purchased from Rieke Metals, Inc. and Nano-C,. Indium-tin oxide (ITO) glass was obtained from Delta Technologies Limited while PEDOT:PSS (Baytron PA14083) was purchased from Bayer Inc.

1. Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl undec-10-enyl malonate (4)

10-undecen-1-ol (5 ml, 0.85 g/ml), triethylene glycol monomethyl ether (4 ml, 1.026 g/ml) and 1 ml pyridine were dissolved into a fresh CH₂Cl₂ (40 ml) in a dry 100 ml nitrogen bottle and equipped with an addition funnel and septum with nitrogen inlet. The solution was stirred at 0 °C for 30 min under a nitrogen atmosphere.

* Corresponding author. Tel.: +86 791 83969562; fax: +86 791 83969561. *E-mail address*: ywchen@ncu.edu.cn (Y. Chen).

Subsequently the malonyl chloride (2.9 ml, 1.45 g/ml) was added dropwise to the mixed solution at 0 °C over the course of 30 minutes under nitrogen atmosphere and the reaction mixture was stirred for 5 hours at room temperature. Then it was extracted by ethyl acetate and water. The combined organic layer was dried over MgSO₄ and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel with ethyl acetate and hexane to give an yellow oil.

¹H NMR (δ, CDCl₃): δ 4.11 (t, 2H), 4.27 (t, 2H).

2. Synthesis of 2-(2-(2-methoxyethoxy) ethoxy) ethyl undec-10-enyl malonate C₆₀ (EEMC)

To a solution of C₆₀ (0.3 g, 0.42 mmol), iodine (0.102 g, 0.42 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.159 g, 1.04 mmol) in toluene (200 ml) was slowly added a solution of compound 4 (0.17 g, 0.42 mmol) in toluene (50 ml). The reaction mixture was stirred at room temperature for 24 hours and sodium thiosulfate aqueous was then added to quench the excessive iodine. The organic was collected and dried by MgSO₄. After removal of the solvent by rotary evaporation, the residue was purified by column chromatography on silica gel with ethyl acetate and toluene to yield 164 mg black solid with 35% yield.

¹H NMR (δ, CDCl₃): δ 4.48 (t, 2H), 4.64 (t, 2H).

Characterization

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 600 NMR spectrometer with deuterated chloroform as the solvent and with tetramethylsilane (δ=0) as the internal standard. The ultraviolet–visible (UV) spectra and optical transmittance spectra of the samples were recorded on a Hitachi UV-3010 spectrophotometer. The UPS measurements were carried out in a Thermo-VG Scientific ESCALAB 250 using a He I (21.22 eV) discharge lamp. A bias of -8.0 V was applied to the samples for separation of the sample and the secondary edge for the analyzer. The HOMO energies are determined by

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

where $h\nu$ is the incident photon energy, $h\nu = 21.22$ eV. E_{cutoff} is defined as the high binding energy cutoff. E_{onset} is the HOMO energy onset, generally referred to as the low binding energy onset. XPS studies were performed on a Thermo-VG Scientific ESCALAB 250 photoelectron spectrometer using a monochromated AlK α (1,486.6 eV) X-ray source. All recorded peaks were corrected for electrostatic effects by setting the C–C component of the C 1s peak to 284.8 eV. The base pressure in the XPS analysis chamber was 2×10^{-9} mbar. Atomic force microscopic (AFM) images were measured on a nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. Scanning electron microscopy (SEM) with gold vapor deposition was made on FEI, QuanTA-200F environmental scanning electron microscope. Current-voltage (J-V) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm^2 simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000).

Device fabrication

All the devices were manufactured with the structure of Glass/ITO/EEMC/ZnO/active layer/MoO $_3$ /Ag. The conductive ITO substrates were cleaned by ultrasonication in acetone, soap water, deionized water and isopropanol. After drying the ITO substrates and treating the surface with UV ozone for 20 minutes, The ZnO precursor solution which was prepared by dissolving zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.9%, 1 g) and ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, 99.5%, 0.28 g) in 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, 99.8%, 10 ml) under vigorous stirring for 12 h was spin-coated onto the cleaned ITO substrates at a spin speed of 4000 rpm for 1 min and then thermal annealed at 245 °C for 1h. For the devices with MT-PEEMC interlayer a solution of EEMC in o-dichlorobenzene (4 mg/ml) was spin-cast on top of the ZnO layer at 4000 rpm for 1 min and dried in the glove box. Subsequently methanol was added atop the EEMC monolayer and the solvent was removed by spin coating at 2500 rpm/40 s after a short wait time. Then the film was heated at 160 °C for 30 min for thermal polymerization in the glove box. P3HT (20 mg/ml) and PCBM

(20 mg/ml) were dissolved in 1 mL of o-dichlorobenzene. Then the P3HT:PCBM blend was spin-cast at 800 rpm/30 s. Thermal annealing was carried out by putting the samples directly on a hot plate at 150 °C for 10 min in a nitrogen filled glove box. The PTB7/PC₇₁BM system (1:1.5 by weight) was spin-coated from a o-dichlorobenzene solution (25 mg/ml) with 3 vol% 1,8-diiodooctane as cosolvent at a speed of 900 rpm/40 s. Then a thin layer of MoO₃ film (9 nm) was evaporated on top of the active layer. Finally, a layer of silver (Ag) (60 nm) was deposited in a vacuum chamber. Additionally, the sol-gel derived VO_x (s-VO_x) was spin-coated from isopropanol solution of vanadium (V) oxitriisopropoxide (Alfa Aesar) at 1:150 ratios. A resulting 10 nm layer thickness was subsequently stored at ambient air for 1 h for hydrolysis at room temperature. All the *J-V* curves of the devices were measured under 100 mW/cm² AM 1.5 solar irradiation in ambient air. The active area of device was 4 mm².

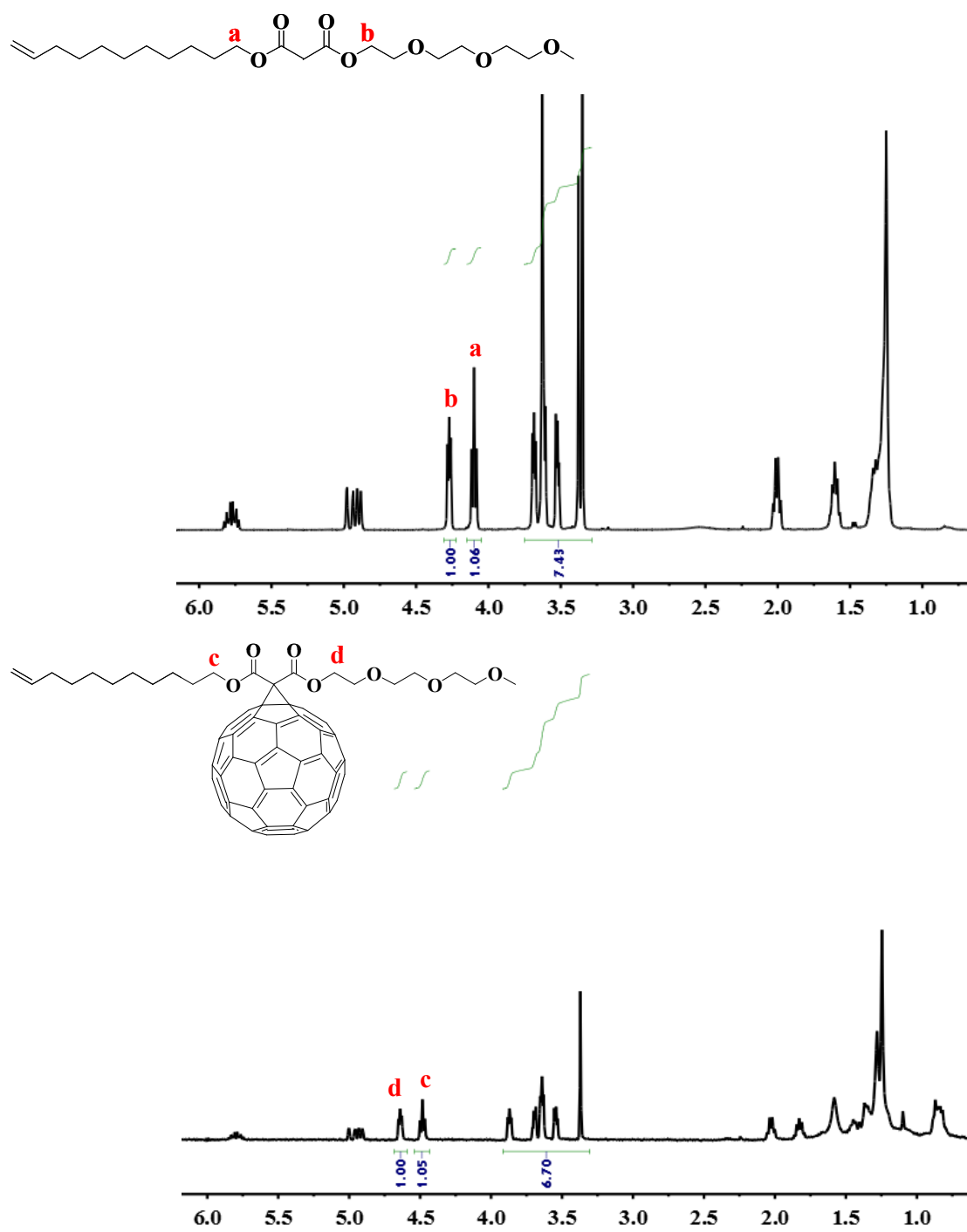


Figure S1. The ^1H NMR of compound 4 and EEMC.

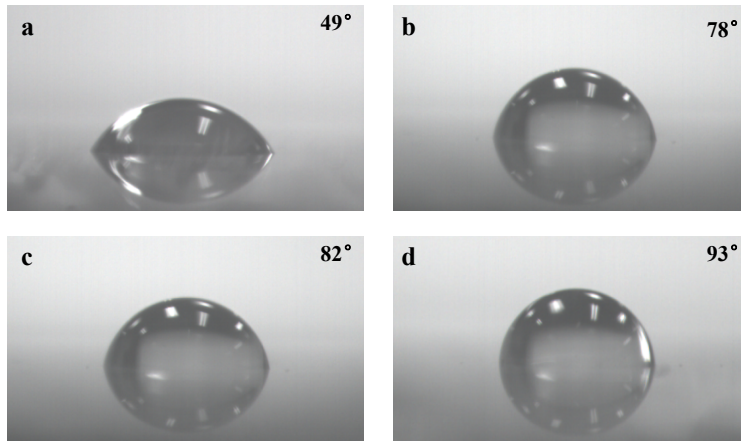


Figure S2. Surface contact angle measurement: **a.** ITO/ZnO; **b.** ITO/ZnO/PEEMC; **c.** ITO/ZnO/MT-PEEMC; **d.** ITO/ZnO/pure C₆₀.

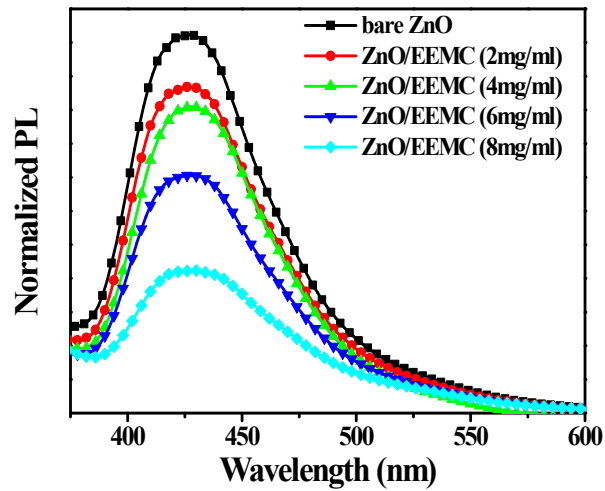


Figure S3. The photoluminescence (PL) spectra of ZnO modified by EEMC with different concentrations.

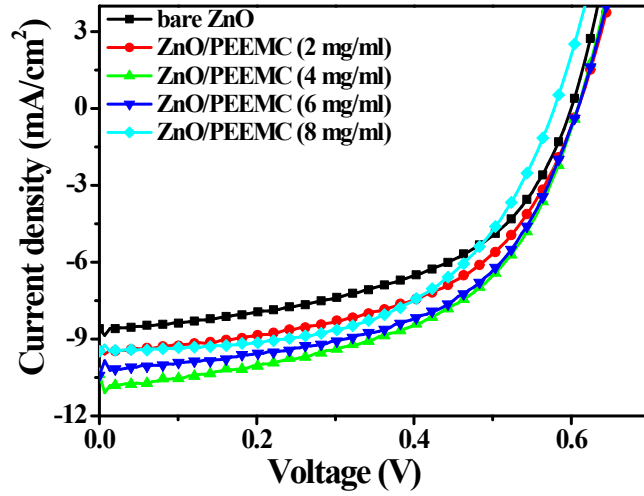


Figure S4. J–V characteristics of the I-PSCs ITO/ZnO/PEEMC/P3HT:PC₆₁BM/MoO₃/Ag with EEMC of different weight concentrations.

Table S1. Performance Parameters of the Inverted Devices based P3HT:PC₆₁BM with EEMC of Different Weight Concentrations as Electron Transport Layers

| ETLs | J_{sc} (mA/cm ²) | V_{oc} (V) | FF (%) | PCE (%) |
|---------------------|--------------------------------|--------------|----------|---------|
| ZnO | 8.59 | 0.599 | 51.7 | 2.7 |
| ZnO/PEEMC (2 mg/ml) | 9.44 | 0.608 | 53.3 | 3.1 |
| ZnO/PEEMC (4 mg/ml) | 10.38 | 0.607 | 54.9 | 3.5 |
| ZnO/PEEMC (6 mg/ml) | 10.42 | 0.607 | 53.5 | 3.4 |
| ZnO/PEEMC (8 mg/ml) | 9.47 | 0.577 | 54.7 | 3.0 |

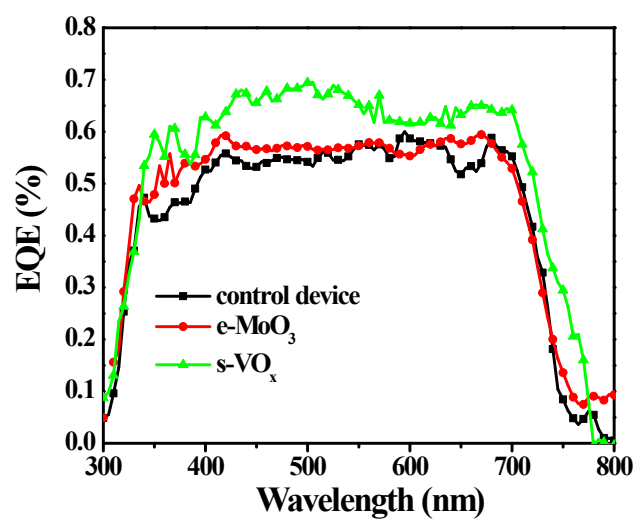


Figure S5. The EQE of the I-PSCs: Device D, ITO/ZnO/PTB7:PC₇₁BM (1:1.5, w/w) /e-MoO₃/Ag; Device E, ITO/ZnO/MT-PEEMC (4 mg/ml)/PTB7:PC₇₁BM (1:1.5, w/w)/e-MoO₃/Ag; Device F, ITO/ZnO/MT-PEEMC (4 mg/ml)/PTB7:PC₇₁BM (1:1.5, w/w)/s-VO_x/Ag.