Electronic Supporting Information

Highly Stable Organic Solar Cells with Robust Interface Using Fullerenol as Molecular Linker

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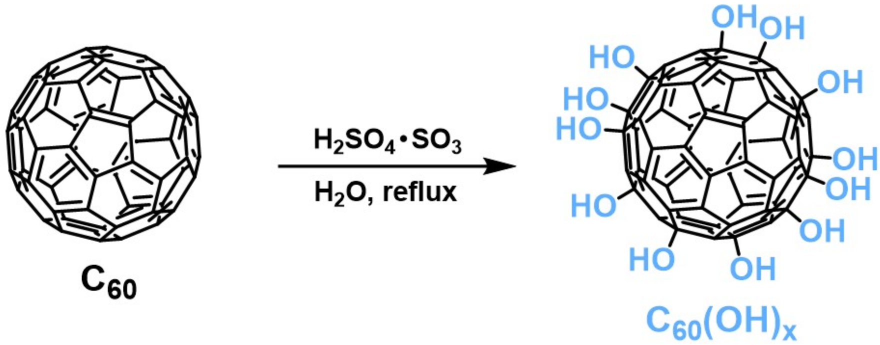
KEYWORDS. Organic solar cells, fullerenol, molecular linker, thermal stability, photo stability



Scheme S1. Synthesis of $C_{60}(OH)_x$.[1-3]

An Erlenmeyer flask (250 mL) was charged with C_{60} (500 mg, 0.69 mmol), followed by dropwise addition of neat fuming sulfuric acid (100 mL) into the flask. The resulting mixture was stirred at room temperature under a nitrogen atmosphere for seven days to obtain a dark brown solution. The mixture was then slowly added into anhydrous diethyl ether in an ice bath to precipitate the solid compound. The resulting intermediate was then combined with distilled water (100 mL) in a round-bottom flask (250 mL) equipped with a condenser and refluxed overnight. The crude product was separated using a Brinell funnel, washed several times with water, and then dried in a vacuum oven at 90 °C to yield 411 mg of product (~65% yield). The above synthesis method was conducted following previously reported literature procedures [1-3]. As mentioned in the literature [1-3], the $C_{60}(OH)_x$ obtained from this method contains an average of 10 to 12 hydroxyl groups on each C_{60} core. ^{1}H NMR (600 MHz, DMSO-d_6): δ 3.527 (OH).

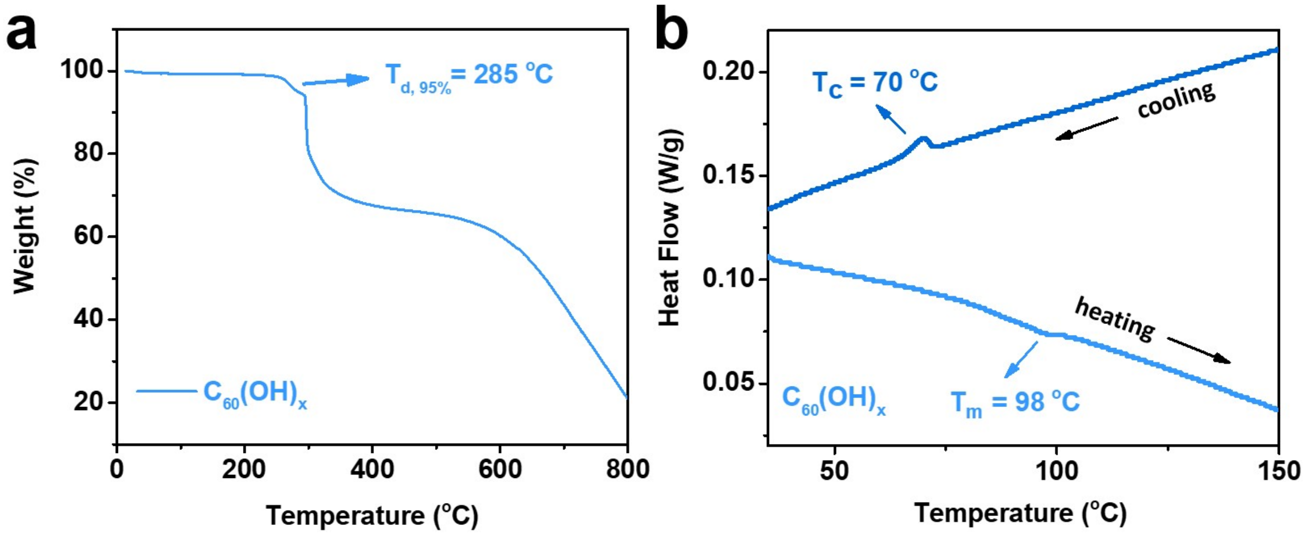


Fig. S1 (a) TGA curve and (b) DSC thermograms of $C_{60}(OH)_x$.

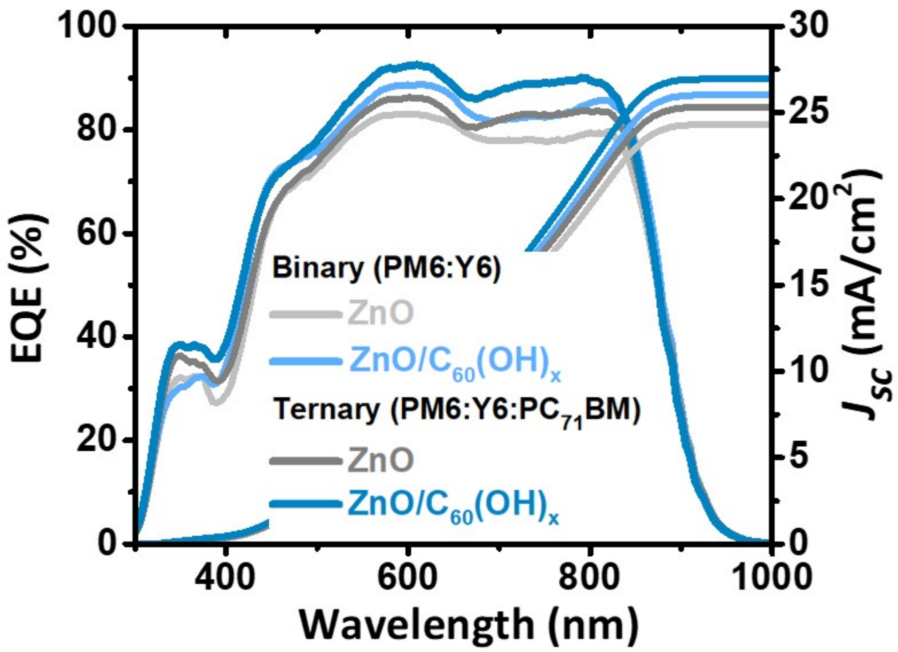


Fig. S2 EQEs spectra and integrated J_{sc} of all devices in this study.

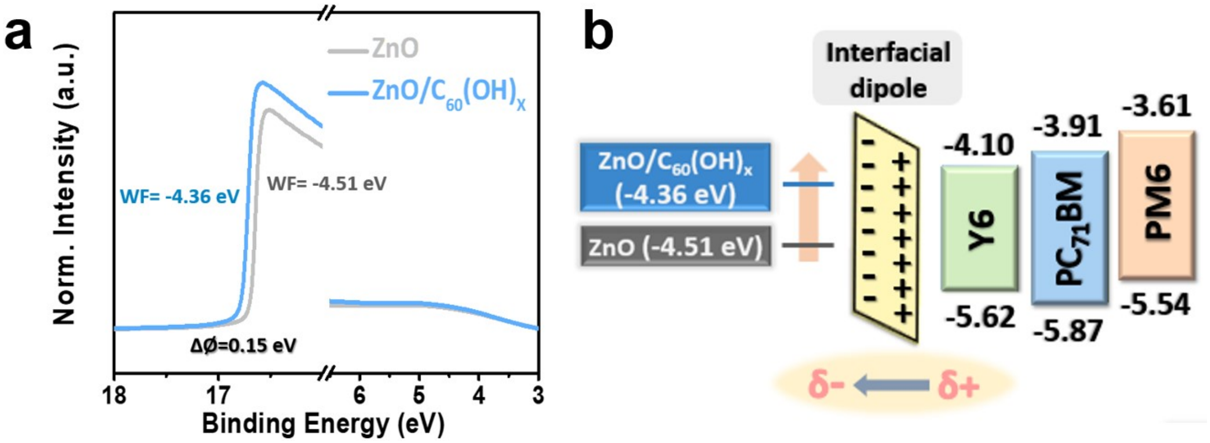


Fig. S3 (a) Characteristics of the ZnO and ZnO/$C_{60}(OH)_x$ films measured by UPS. (b) Schematic illustration of the energy-level diagram in this study.

Table S1 The parameters τ_1 and τ_2 of biexponential decay fitting for the TRPL results

ETLs	τ_1 Lifetime (ns)	τ_2 Lifetime (ns)
ZnO	1.46	2.00
ZnO/$C_{60}(OH)_x$	1.09	1.44

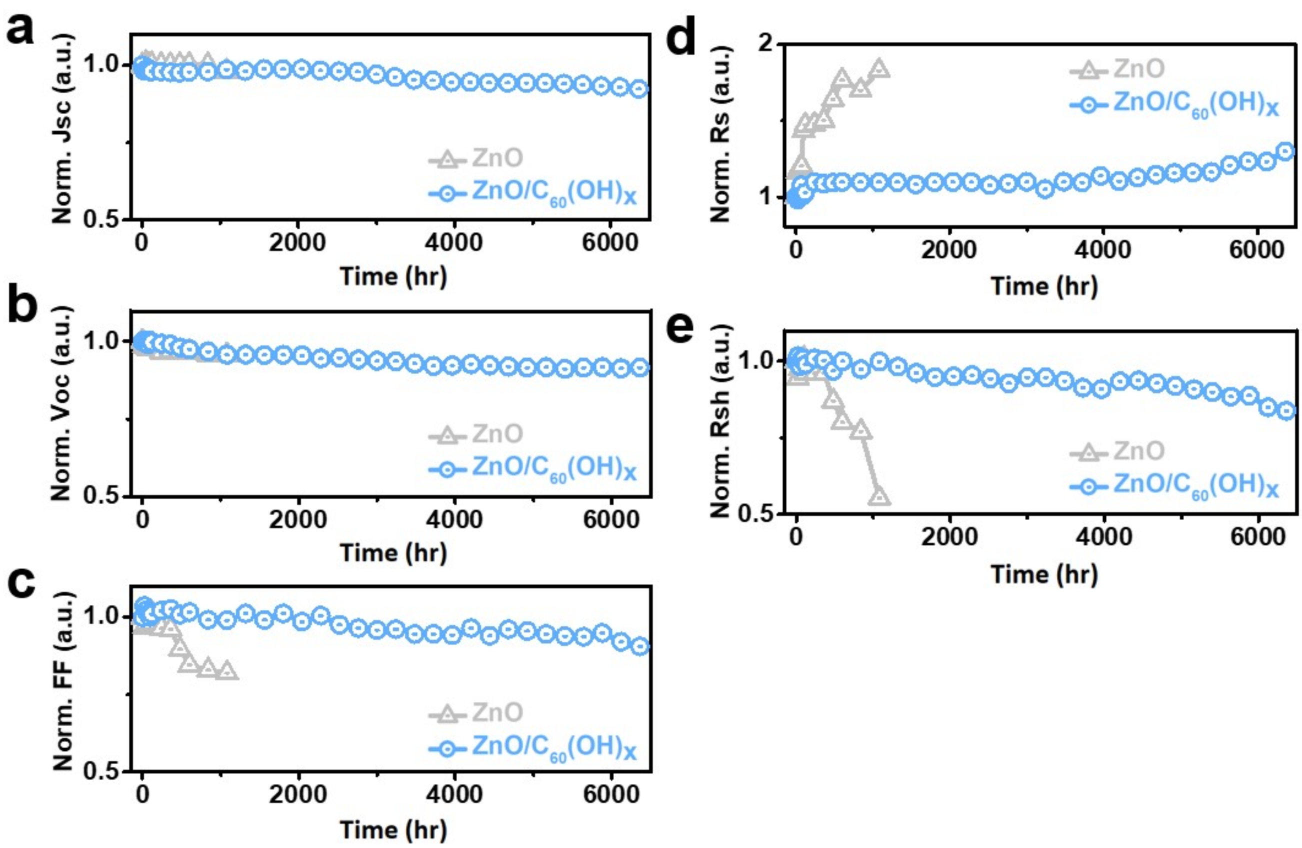


Fig. S4 The evolutions of normalized (a) J_{sc}, (b) V_{oc}, (c) FF, (d) R_s, and (e) R_{sh} of the studied OSCs under thermal aging at 65 °C in N_2.

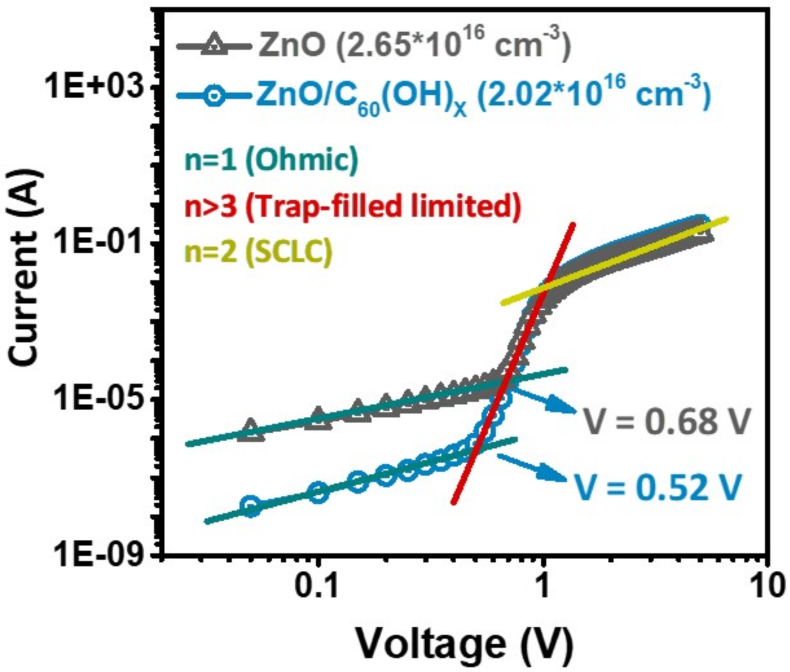


Fig. S5 Current-voltage traces and trap density of ZnO and $ZnO/C_{60}(OH)_x$ devices. [4] These devices were thermally annealed at 65 °C for 800 hr in N_2 prior measurement.

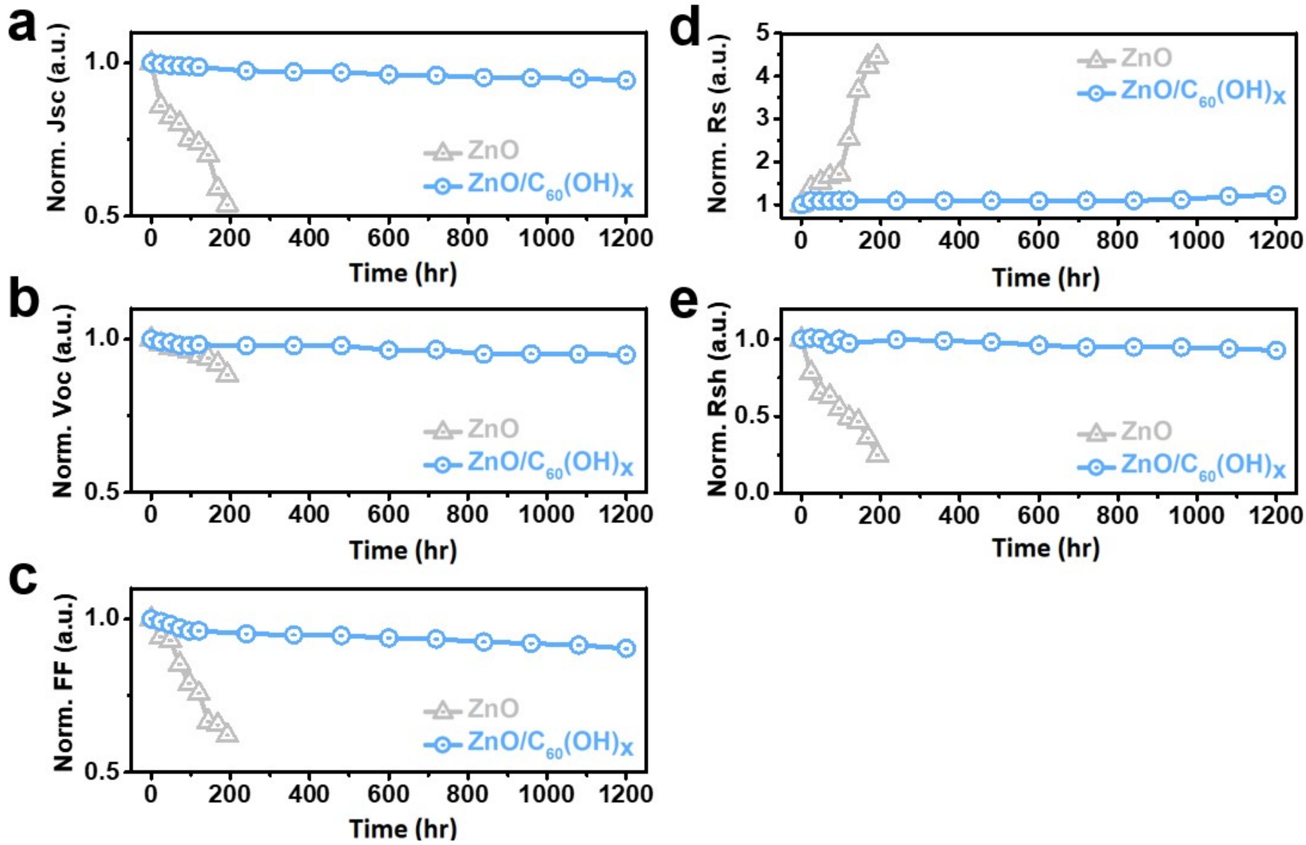


Fig. S6 The evolutions of normalized (a) J_{sc}, (b) V_{oc}, (c) FF, (d) R_s, and (e) R_{sh} of the studied OSCs during continuous light soaking under AM 1.5G simulated solar light at one-sun intensity in N_2.

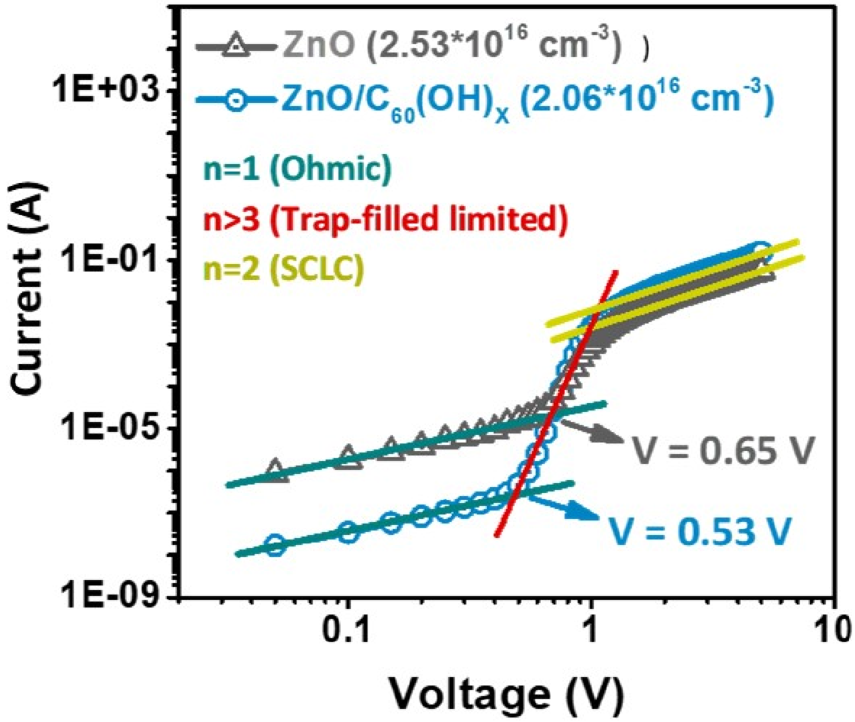


Fig S7 Current-voltage traces and trap density of ZnO and $ZnO/C_{60}(OH)_x$ devices. [4] These devices were continuously illuminated with AM 1.5G simulated solar light at one-sun intensity for 120 hr in N_2 before measurement.

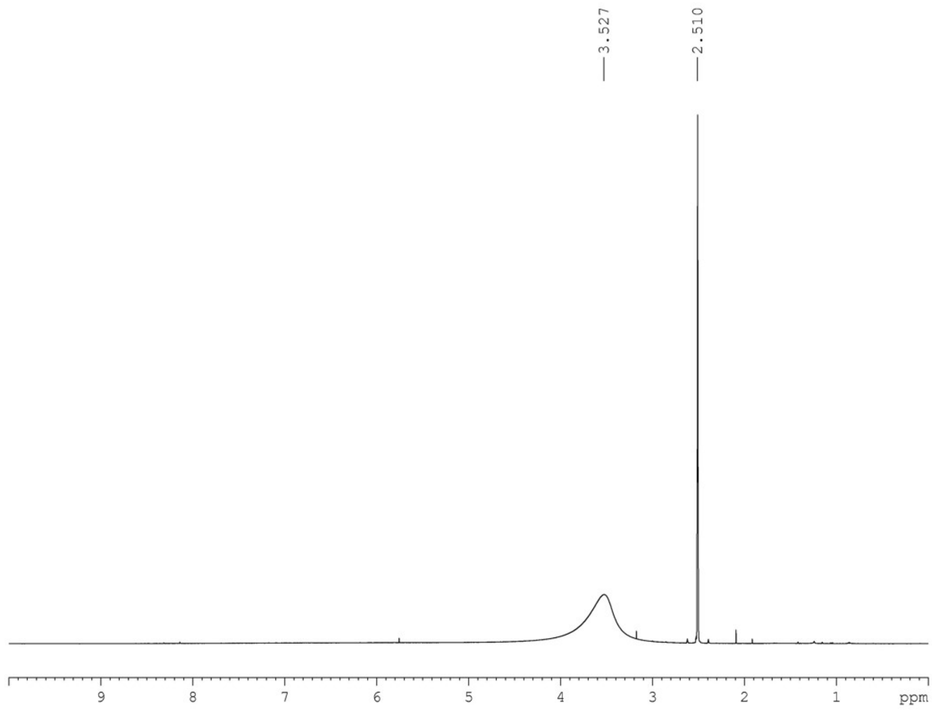


Fig S8 ^{1}H-NMR spectrum of $C_{60}(OH)_x$.

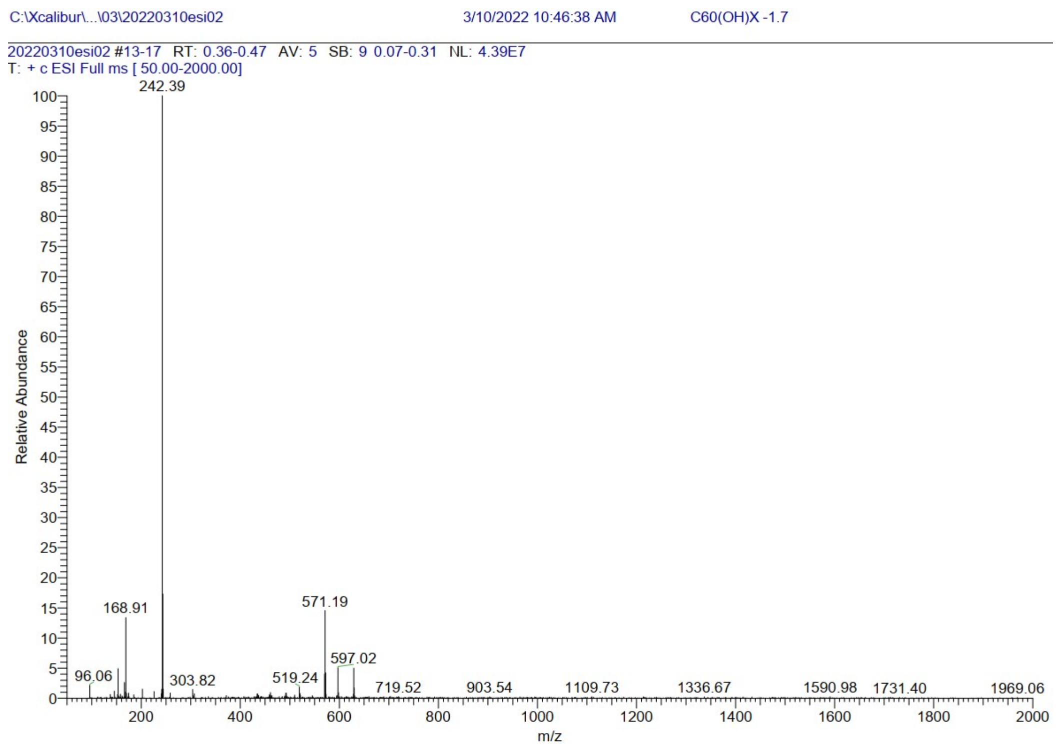


Fig S9 Mass spectrum of $C_{60}(OH)_x$.

EXPERIMENTAL SECTION

Materials. PM6 and Y6 were obtained from WAYS Technical Corp., Ltd. (Taiwan) and were used without additional purification. Molybdenum trioxide (MoO_3), chloroform (CF), *N*, *N*-dimethylformamide (DMF), 1-chloronaphthalene (CN), chlorobenzene (CB), deuterated dimethyl sulfoxide (DMSO-d_6), 2-methoxyethanol, and ethanolamine were purchased from Sigma-Aldrich. C_{60} and $PC_{71}BM$ were purchased from 1-Materials (Canada).

Device Fabrication. Inverted OSCs were constructed with the configuration ITO glass/ZnO or ZnO/$C_{60}(OH)_x$/photoactive layer/MoO_3/Ag. The ITO-coated glass substrates underwent ultrasonic cleaning in detergent, deionized water, acetone, and isopropanol, each for 30 minutes. Following this, the substrates were dried using N_2 flow and subjected to plasma treatment for 10 minutes. For the ZnO layer, a precursor solution was made by dissolving 100 mg of zinc acetate in 1.0 mL of 2-methoxyethanol, with 28 μL of ethanolamine added. This ZnO precursor was spin-coated onto the ITO substrates at 4000 rpm for 30 seconds and then annealed at 220°C for 30 minutes in ambient air. The $C_{60}(OH)_x$ solution, with a concentration of 0.1 mg/mL, was prepared using DMF as the solvent. This solution was spin-coated onto the ZnO layer at 4000 rpm for 1 minute and then annealed at 140°C for 10 minutes in ambient air. The thickness of the $C_{60}(OH)_x$ was estimated using a Surface Profiler (α-stepper) to be around 1 to 2 nm. For the photoactive layer, the precursor solution for the PM6:Y6 bulk heterojunction (BHJ) blend, in a 1:1.2 weight ratio, was prepared in CF with 0.5% volume ratio of CN. This solution was spin-coated onto the ZnO or ZnO/$C_{60}(OH)_x$ electron transport layers (ETLs) at 3000 rpm for 40 seconds and annealed at 110°C for 10 minutes in N_2. Similarly, the precursor solution for the PM6:Y6:$PC_{71}BM$ BHJ blend, in a 1:1.2:0.2 weight ratio, was prepared in CF with a 0.75% volume ratio of CN. This solution was spin-coated onto the ZnO or ZnO/$C_{60}(OH)_x$ ETLs at 3000 rpm for 40 seconds and annealed at 90°C for 10 minutes in N_2. Finally, 8 nm of MoO_3 and 100 nm of Ag were sequentially thermally deposited under high vacuum ($<10^{-6}$ Torr) to form the top electrode. The active area of each device was 0.07 cm².

and reverse scan between −□.□ and □.□ V with a voltage step of □.□□ V and delay time of □□ ms by a Keithley □□□□ source meter (Keithley Instrument. Inc.). The photovoltaic performance measurements were conducted under one-sun intensity (□□□ mW cm −□) using a Xenon-lamp based solar simulator calibrated with AM□.□G spectrum (Enli Tech.). The intensity of the solar spectrum was calibrated by a SRC□□□□ monocrystalline sili-

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Characterization. IR spectra were recorded with a JASCO 4100 FT-IR spectrometer, and UV-vis absorption spectra were measured using a JASCO V-670 spectrometer (JASCO Company, Hachioji, Tokyo, Japan). Photoluminescence (PL) spectra were obtained with an Edinburgh PLS 920. For time-resolved PL decay curves, a time-correlated single photon counting (TCSPC) method was utilized. The sample was illuminated with a 485 nm laser head (LDH-P-C-485) from PicoQuant GmbH, driven by a picosecond pulsed diode laser driver (PDL 800-B) from the same company, operating at 2.5 MHz with a 400 ns pulse duration and a fluence of approximately 25.4 μW cm^{-2}. The PL signal was detected using an ultralow noise single photon avalanche detector (ID-100-50) from Becker & Hickl GmbH. External quantum efficiency (EQE) measurements were carried out with monochromatic light from a xenon lamp (QE-R, Enlitech Co., Ltd.), and light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell from 300 to 800 nm. Electrochemical impedance spectroscopy (EIS) was performed with a Metrohm Autolab PGSTAT 320N, applying a small AC perturbation voltage of 15 mV to the devices and measuring the output currents across a frequency range of 1 MHz to 1 Hz. X-ray photoelectron spectroscopy (XPS) was conducted with a Theta Probe Angle-Resolved X-ray Photoelectron Spectrometer using Al-Kα X-ray photons (hυ = 1486.6 eV). Current-voltage (*J-V*) characteristics were measured using a Keithley 2400 source meter (Keithley Instruments, Inc.) with a voltage scan from -0.05 to 1 V, a step of 0.01 V, and a delay time of 10 ms. Photovoltaic performance was assessed under one-sun intensity (100 mW cm^{-2}) with a Xenon-lamp based solar simulator calibrated to the AM1.5G spectrum (Enlitech). The solar spectrum intensity was calibrated using the SRC 2020 monocrystalline silicon solar cell (Enlitech). The mass analysis was performed using Orbitrap QE Plus Mass Spectrometry. ^{1}H NMR were recorded on a Bruker Avance III HD-600 MHz using DMSO-d_7 as the solvent. The thermal properties of the samples were characterized using a PerkinElmer DSC 8000 instrument under a nitrogen atmosphere, with a heating/cooling cycle ranging from 25 to 150 °C at a rate of 10 °C/min. Thermogravimetric analysis (TGA) was conducted using a HITACHI STA 7200 thermogravimetric analyzer, with samples heated from 25 to 800 °C at a rate of 10 °C/min in a nitrogen environment. Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted using an ULVAC-PHI PHI 5000 Versaprobe II electron spectroscopy for chemical analysis system, with a He (I) (21.22 eV) light source.

Stability testing. The thermal stability of the devices was examined by subjecting them to constant heat stress in N_2 within a glovebox. For the light-soaking test, the devices were exposed to AM 1.5G simulated solar light (LSH-7320, Newport, Bozeman, USA) at one-sun intensity in N_2.

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