

An Efficient Interface Modification Material for Improved Efficiency and Stability in Inverted Organic Solar Cells

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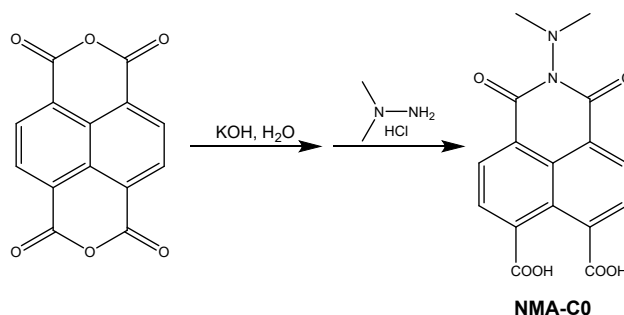
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1. Materials and Methods.

1.1 Materials.

PM6 was purchased from Solarmer Materials, Inc. L8-BO was provided by Jiaxing Hyper Optoelectronic Technology Co., Ltd. The materials required for the synthesis of NMA-C0 (isochromeno[6,5,4-def]isochromene-1,3,6,8-tetraone, 1,1-dimethylhydrazine hydrochloride, Potassium hydroxide and Phosphoric acid) were purchased from Grass (Tianjin) Technology Co., Ltd.

1.2 Synthesis



1 M potassium hydroxide aqueous solution (10 mL) was added to a solution of isochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (500 mg, 1.86 mmol) in distilled water (100 mL) at room temperature until the solution was clear. Then 1 M phosphoric acid aqueous solution was added to adjust the pH to 6.4. 1,1-dimethylhydrazine hydrochloride (215 mg, 2.24 mmol) was dissolved in 1 M potassium hydroxide aqueous solution and then added to the reaction mixture, followed by 1 M phosphoric acid aqueous solution was added to adjust the pH to 6.4. The reaction mixture was refluxed for 72 h under Ar atmosphere. After cooling to room temperature, the reaction was filtered and acetic acid was added to the filtrate to adjust pH to 4. The reaction mixture was extracted with ethyl acetate (5×40 mL) and the organic phase was washed with brine (3×90 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to remove the solvent. The product was filtered from the cold ethyl acetate and dried under vacuum to afford 2-(dimethylamino)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6,7-dicarboxylic acid (**NMA-C0**) (200 mg, 32.67% yield) as a yellow solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.54 (s, 2H), 8.53 (d, *J* = 7.5 Hz, 2H), 8.18 (d, *J* = 7.5 Hz, 2H), 2.95 (s, 6H). **¹³C NMR** (100 MHz, DMSO-*d*₆): δ (ppm) 168.4, 162.5, 136.4, 129.9, 129.2, 128.3, 125.8, 125.4, 43.2. **HRMS** (m/z, ESI): calculated for C₁₆H₁₂N₂O₆ [M]⁻: 327.0695, found: 327.0620.

1.3 Measurements and characterization

Device fabrication

The OSCs devices were fabricated using an inverted structure of ITO/ZnO or ZnO/NMA-C0/active layers/MoO_x/Ag. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by a nitrogen blow. Subsequently, ZnO (~15 nm) was deposited by spin-coating a ZnO precursor solution (prepared by dissolving 100 mg zinc acetate dihydrate and 28 μl ethanolamine in 4 ml of 2-methoxyethano) on the top of the ITO glass substrates at 3000 rpm for 30 s. After being baked at 200 °C in air for 1 h, the ZnO-coated substrates were transferred into a nitrogen-filled glove box. For the hybrid ETL of ZnO/NMA-C0, the NMA-C0 film was deposited upon ZnO film from its solution with a concentration of 0.4 mg/ml in methyl alcohol, and then baked on a hot plate at 120 °C for 10 min in ambient atmosphere. Then the PM6:L8-BO mixtures (D:A ratio=1:1.2) were fully dissolved in chloroform (CF) with 0.25% 1,8-Diiodooctane (DIO) as an additive at a total concentration of 15.4 mg mL⁻¹. The blend solutions was spin-casted at 3000 rpm onto the ETL. After spin-coating, the blended films were annealed at 100 °C for 10 mins. Then, MoO_x (~2 nm) and Ag (~150 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10⁻⁴ Pa).

Device characterization (*J-V*, EQE).

The current density-voltage (*J-V*) characteristics of photovoltaic devices were obtained using a Keithley 2400 source measure unit, the scan speed and dwell times of the *J-V* curves were fixed at 0.02 V s⁻¹ and 20 ms, respectively. The photocurrent was measured

under illumination simulated 100 mW cm^{-2} AM1.5G irradiation using an SS-X50 solar simulator, calibrated with a standard Si solar cell (Enli Technology Co., Ltd., Taiwan, and calibrated report can be traced to NREL). The external quantum efficiency (EQE) spectrum was measured using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan).

Operation stability test.

The devices were placed under continuous light, which generated by the LED system (MT-PV-64, TIANJIN METO) at $25 \pm 2 \text{ }^\circ\text{C}$ in N_2 atmosphere without encapsulation. The stabilized PCE was periodically measured 1 sun illumination at 16 independent channels with MPPT. The JV values were recorded using the multimeter (Mato-30) and software.

Thermal stability test.

All devices were fabricated under optimized processing conditions. Devices for thermal stability test were placed in N_2 atmosphere without encapsulation and carried out on a hot plate (WH200D-1K, WIGGENS, Germany) with a continuous thermal stress of $65 \text{ }^\circ\text{C}$ in dark condition.

Ultraviolet photoelectron spectroscopy (UPS) measurement.

UPS experiments were carried out by PHI 5000 Versaprobe III in ultrahigh vacuum with a base pressure of $1 \times 10^{-6} \text{ Pa}$. Xray source is He I 21.2 eV UPS at 0.0 W, and the Beam diameter is 5.0 μm , using the FAT Analyzer mode.

Electrochemical impedance spectroscopy (EIS) measurement.

The electrochemical impedance spectroscopy (EIS) measurement was performed using Zennium-E. A bias voltage equal to V_{oc} was applied to offset the total current.

Atomic force microscopy (AFM) measurements.

AFM measurement was performed by using a Bruker Dimension icon in ScanAsyst

mode. Film samples were spin-cast under the same conditions as those used for device fabrication.

Transient photocurrent (TPC) and Transient photovoltage (TPV) measurements.

TPC and TPV measurements were performed on a Moxe 180081-4320 with light intensity about 0.5 sun, Voltage and current dynamics were recorded on a digital oscilloscope (Tektronix MDO4104C). Voltages at open circuit and currents under short circuit conditions were measured over a 50 Ω and a 1 M Ω resistor, respectively.

Fabrication of devices for the conductivity measurements.

The conductivity of ETLs is estimated by measuring the current-voltage (I-V) curves of the devices with the sandwich structure ITO/ETL(20 nm)/Ag based on Ohm's law. The I-V characteristics of these devices were measured in the dark.

¹H and ¹³C NMR spectra. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ¹H NMR and ¹³C NMR spectra were referenced to TMS (0 ppm).

High resolution mass spectrum. High resolution mass spectrum was collected on a Varian 7.0T FTMS.

Ultraviolet-visible (UV-Vis) absorption spectrum. UV-Vis absorption spectra were measured on a UV-Vis instrument Agilent Cary 5000 UV-vis-NIR spectrophotometer.

2. Supporting Tables and Figures

Table S1 Photovoltaic parameters of the optimized PM6:L8-BO based devices with ZnO or ZnO/NMA-C0 as the ETL under the illumination of AM 1.5G (100 mWcm⁻²)

ETL ^{a)}	V_{oc} (V)	J_{sc} (mA cm ⁻²)	$J_{sc}^{cal\ b)}$ (mA cm ⁻²)	FF (%)	PCE (%)
ZnO	0.825 (0.825±0.003)	27.09 (26.80±0.24)		73.08 (73.12±0.24)	16.33 (16.16±0.11)
ZnO/NMA-C0	0.827 (0.827±0.002)	28.16 (28.03±0.09)	26.84	73.37 (73.40±0.19)	17.09 (17.01±0.07)

a) The average photovoltaic parameters calculated from 5 independent devices; b) Current densities calculated from EQE curves.

Table S2 Retention rates of V_{oc} (V_{oc}^t/V_{oc}^0), J_{sc} (J_{sc}^t/J_{sc}^0), FF (FF^t/FF^0) and PCE (PCE^t/PCE^0) of PM6:L8-BO based devices with ZnO or ZnO/NMA-C0 as ETL. The parameter “t” is the total heating time during the thermal stability test or total illumination time during the operation stability test.

Test	ETL	t (h)	V_{oc}^t/V_{oc}^0	J_{sc}^t/J_{sc}^0	FF^t/FF^0	PCE^t/PCE^0
operation stability	ZnO	30	90.7%	95.5%	94.6%	81.9%
	ZnO/NMA-C0	241	97.7%	100.1%	94.6%	92.5%
thermal stability	ZnO	1150	95.1%	92.9%	87.2%	77.4%.
	ZnO/NMA-C0	1150	99.3%	97.7%	93.6%	91.2%

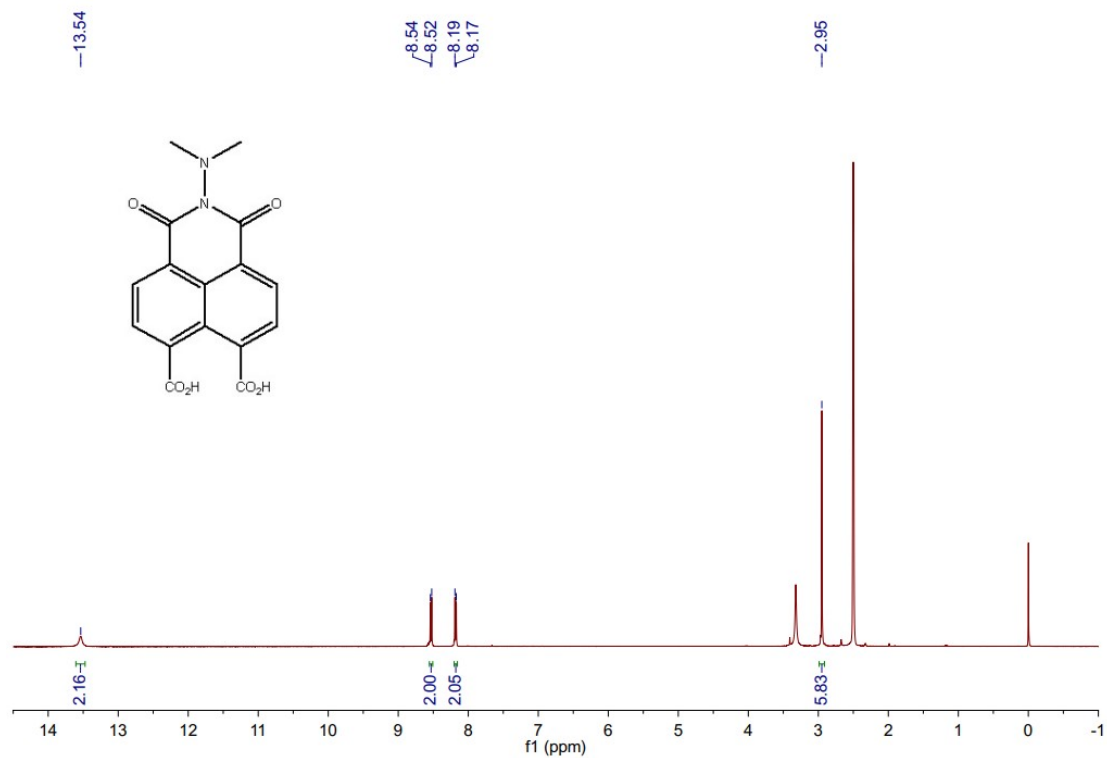


Figure S1 $^1\text{H NMR}$ of NMA-C0

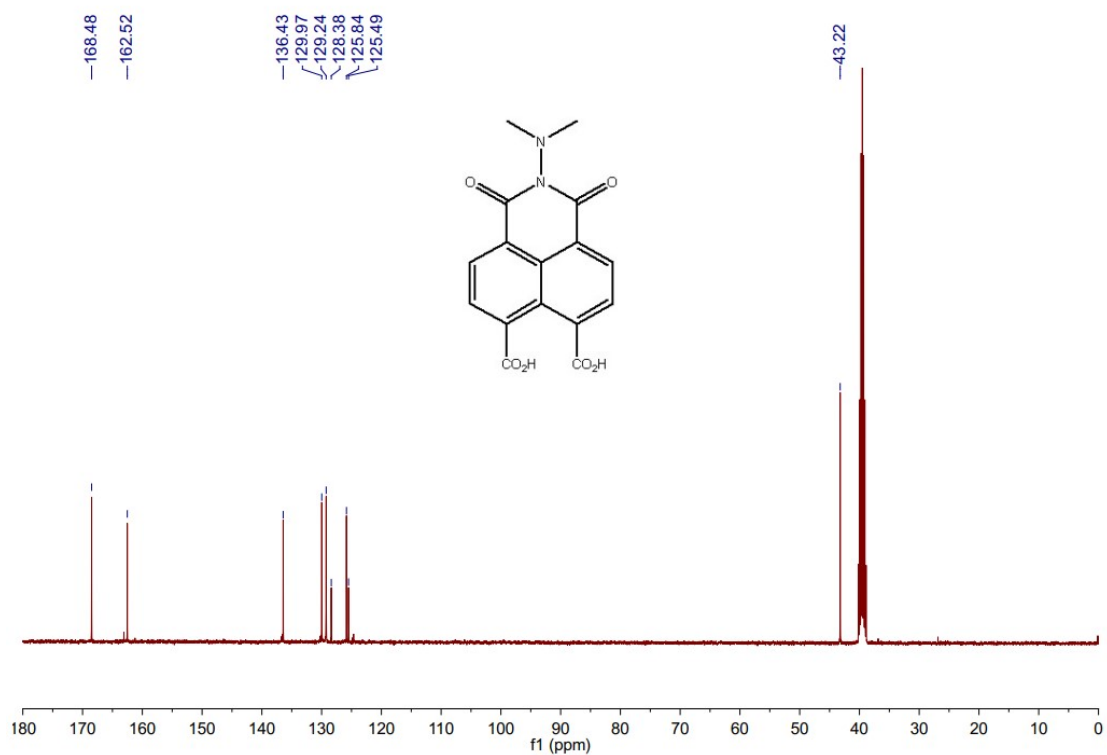


Figure S2 $^{13}\text{C NMR}$ of NMA-C0

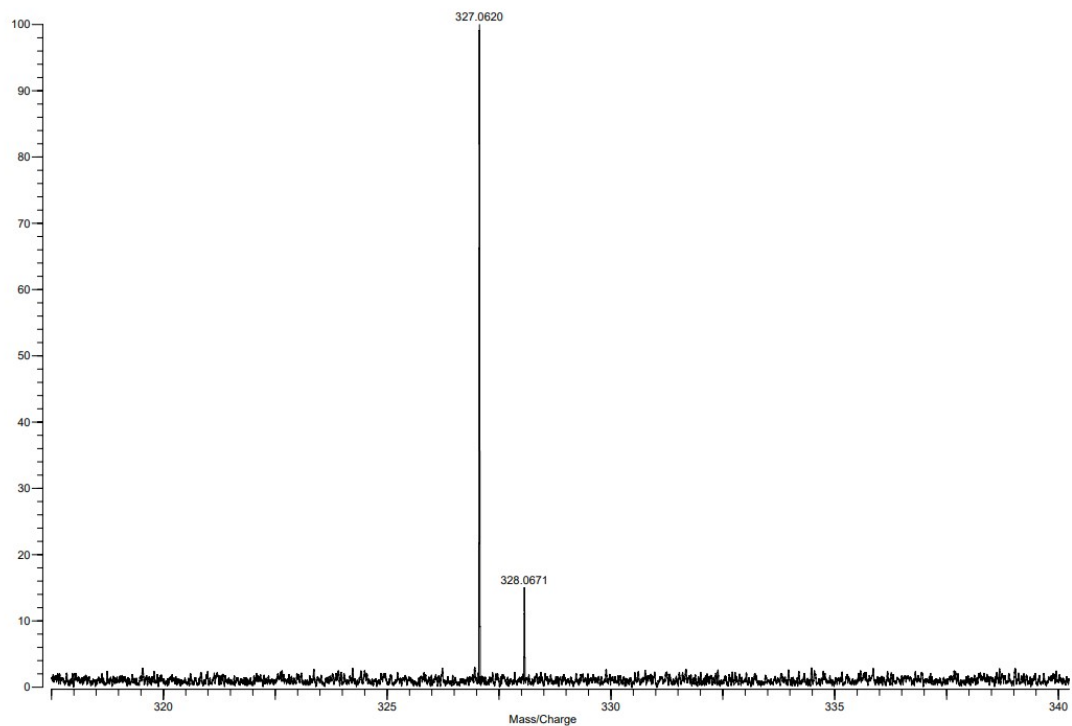


Figure S3 HRMS spectrum of NMA-C0

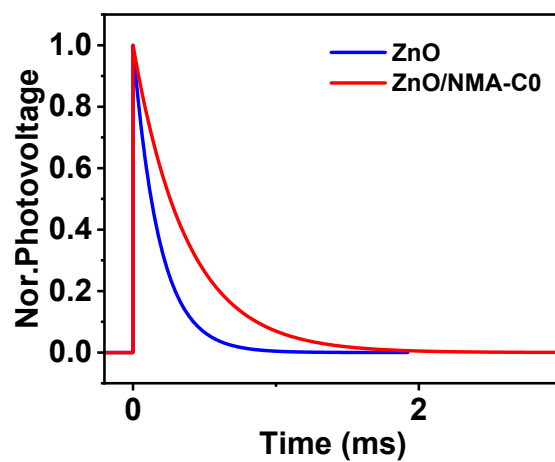


Figure S4 Transient photovoltage measurements of devices based on ZnO or ZnO/NMA-C0 ETL analyzed by a one order exponential decline model.

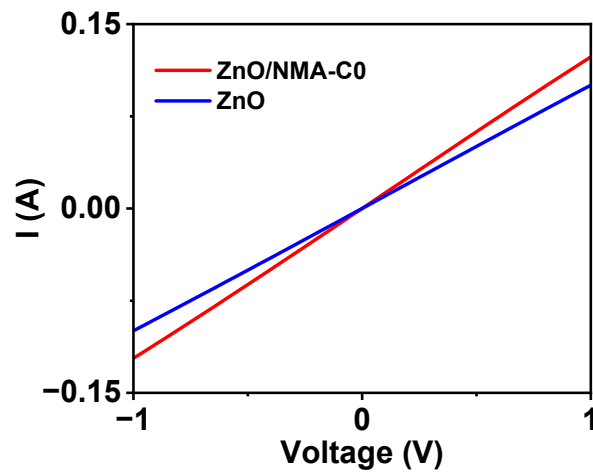


Figure S5 I-V characteristics of ITO/ETLs/Ag devices.

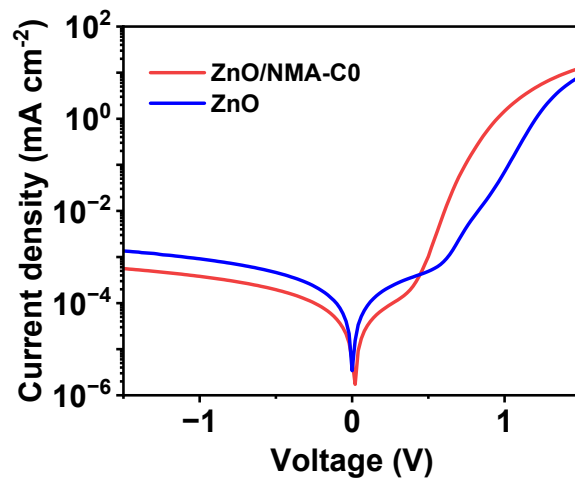


Figure S6 J-V characteristics in the dark of devices based on ZnO or ZnO/NMA-C0.

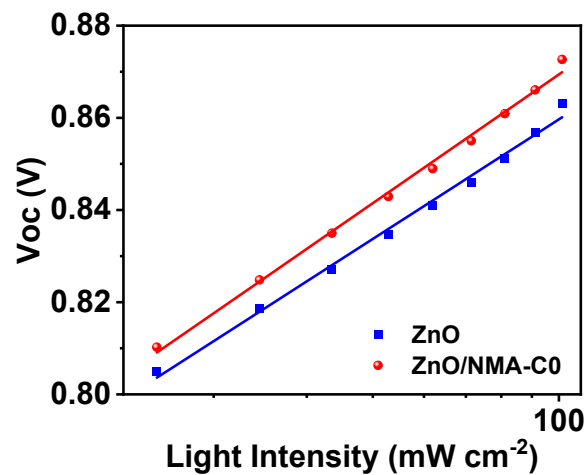


Figure S7 V_{oc} values of the photovoltaic devices versus light intensity.