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Supporting Information

Interface Engineering by a Neutral Carbolong Complex for Efficient and Stable *p-i-n* Perovskite Solar Cells

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Materials and methods

Methylammonium bromide (MABr, >99.95%), formamidinium iodide (FAI, >99.95%), lead (II) bromide ($PbBr_2$, 99.99%), 1,4-butanediammonium iodide (BDAI, >99.9%) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA, Mn=6,000-15,000) were purchased from Xi'an Polymer Light Technology Corp. (China). Indium Tin Oxide (ITO) glasses and lead (II) iodide (PbI_2, 99.999%) were purchased from Advanced Election Technology Co., Ltd. (China). Phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$, 99.5%) was purchased from Shanghai Da Ran Chemicals (China). Chlorobenzene (CB), dimethyl sulfoxide (DMSO), N, N-dimethylformamide (DMF), and anhydrous ethanol were purchased from *J&K*. Copper (Cu, 99.99%) were purchased from commercial sources. Dichloromethane from calcium hydride under N_2 prior to use. The reagents were used as received from commercial sources without further purification. NMR spectroscopic experiments were performed on a Bruker AVIII-600 (^1H, 600.1, ^{13}C, 150.9, ^{31}P, 242.9 MHz) spectrometer at room temperature. The ^1H and ^{13}C NMR chemical shifts (δ) are reported relative to tetramethylsilane, and the ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). HRMS experiments were performed on a Bruker En Apex Ultra 7.0T FT-MS.

Solutions preparation. FAI 216.68 mg, PbI_2 626.97 mg, MABr 15.68 mg, and $PbBr_2$ 51.38 mg were weighed in a vial in glovebox. To them was added 1 mL mixed solvent of DMF and DMSO with volume ratio of 4/1. The solution was stirred at 65 °C for 60 minutes, and to them was added 40 μL of the CsI solution (519.62 mg CsI dissolved in 1 mL DMSO). The mixed precursor was stirred at 65 °C for 15 min before use. PTAA solution was prepared by dissolving 6 mg PTAA into 2 mL CB and stirring for 1 h. $PC_{61}BM$ solution was prepared by weighing 30 mg of $PC_{61}BM$ into 1.5 mL CB and stirring at 70 °C for 2 h. 20 mg BDAI were dissolved in 1 mL CB.

Fabrication of PSCs. ITO glasses were cleaned using detergent, acetone and isopropanol under sonication for 20 minutes respectively. The ITO glasses were dried with nitrogen and treated by air plasma for 4 minutes before transferring into glove box for further spin-coating procedures. PTAA was spin-coated at 6000 rpm for 30 s and annealed at 100 °C for 10 minutes. 20 mg mL^{-1} BDAI was spin-coated at 4000 rpm for 30 s without post-annealing. Perovskite precursor was deposited by spin-coating at 1000 rpm for 10 s and then 5000 rpm for 30 s. 250 μL CB were splashed at 8 s before the end of the high-speed step. The substrate was immediately annealed at 100 °C for 20 min. $PC_{61}BM$ was spin-coated on perovskite layer at 1000 rpm for 45 s. Ethanol solution with different concentrations of NC was spin-coated at 5000 rpm for 60 s. 100 nm Cu was deposited in the thermal evaporator. The device area of 0.04 cm^2 is defined by a photomask.

Characterizations. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyser, which has a furnace containing a sample pan supported by a precision balance. The film surface topography images were recorded with the Atomic Force Microscopy (AFM, Asylum Research MFP-3D-Stand Alone). The Ultraviolet Photoelectron Spectroscopy (UPS) was performed with a non-monochromated He Iα photon source (hv=21.22 eV). A Source Meter (Keysight B2901A) and a solar simulator (Enlitech SS-F5-3A) were used to measure the current density-voltage (*J-V*) curves. The device *J-V* curves were measured with 10 mV intervals and 10 ms delay time under AM 1.5 G at 100 mW cm^{-2} light intensity illumination. The external quantum efficiency (EQE) spectra were recorded with a quantum efficiency measuring facility (Enlitech QER-3011), in which the light intensity at every measured wavelength was calibrated with a standard Silicon photodiode. Maximum-power-point tracking (MPPT) were collected by measuring the steady-state current density at the MPP voltage. All the above device measurements were performed in a nitrogen filled glove box. Transient photocurrent (TPC) measurements were carried out with a self-build system, where the solar cells were excited by a 532 nm incident laser (SpitLight Compact IOO) and a digital oscilloscope (Keysight) was used to record the photocurrent decay signal of the sample. Electrochemical impedance spectroscopy (EIS) was performed with the frequency range from 200 Hz to 2 MHz by the electrochemical workstation (Princeton Applied Research, P4000+).

Preparation and characterization of NC

To a red solution of **a1** (362 mg, 0.33 mmol) in dichloromethane (10 mL) was added trimethylamine-N-oxide dihydrate (37 mg, 0.33 mmol) and tetrabutylammoniumchloride (92 mg, 0.33 mmol). The reaction mixture was stirred at room temperature for *cal.* 8 h to give a deep brown solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography (silica gel, 200-300 mesh elute: acetone/dichloromethane = 1:30) to give **NC** as a brown solid. Yield: 262 mg, 78%.

^{1}H NMR (600.1 MHz, CD_2Cl_2): δ = 12.66 (s, 1H, C7*H*), 10.86 (br, 1H, C1*H*), 7.41-7.21 (30H, Ph), 7.01 (d, *J*(PH) = 3.2 Hz, 1H, C3*H*), 4.99 (br, 1H, O*H*), 3.66 (s, 6H, COOCH_3), 3.33 (br, 2H, C11*H*), 1.82 ppm (br, 2H, C9*H*); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ = -12.55 ppm (s, Ir*P*Ph_3); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC): δ = 200.1 (t, *J*(PC) = 10.6 Hz, C7), 176.8 (t, *J*(PC) = 3.2 Hz, C2), 172.2 (s, *C*OOMe), 171.8 (t, *J*(PC) = 3.6 Hz, C4), 170.0 (s, C6), 168.8 (t, *J*(PC) = 12.0 Hz, C1), 163.4 (s, C5), 138.1 (s, C3), 134.9-126.9 (m, Ph), 64.2 (s, C9), 52.7 (s, COO*C*H_3), 38.8 (s, C8), 37.9 ppm (s, C10); HRMS (ESI): m/z calcd for $[M-Cl]^+$: $[C_{50}H_{44}IrO_5P_2]^+$, 979.2288; found, 979.2293.

Spectroscopic and HRMS Data of NC:

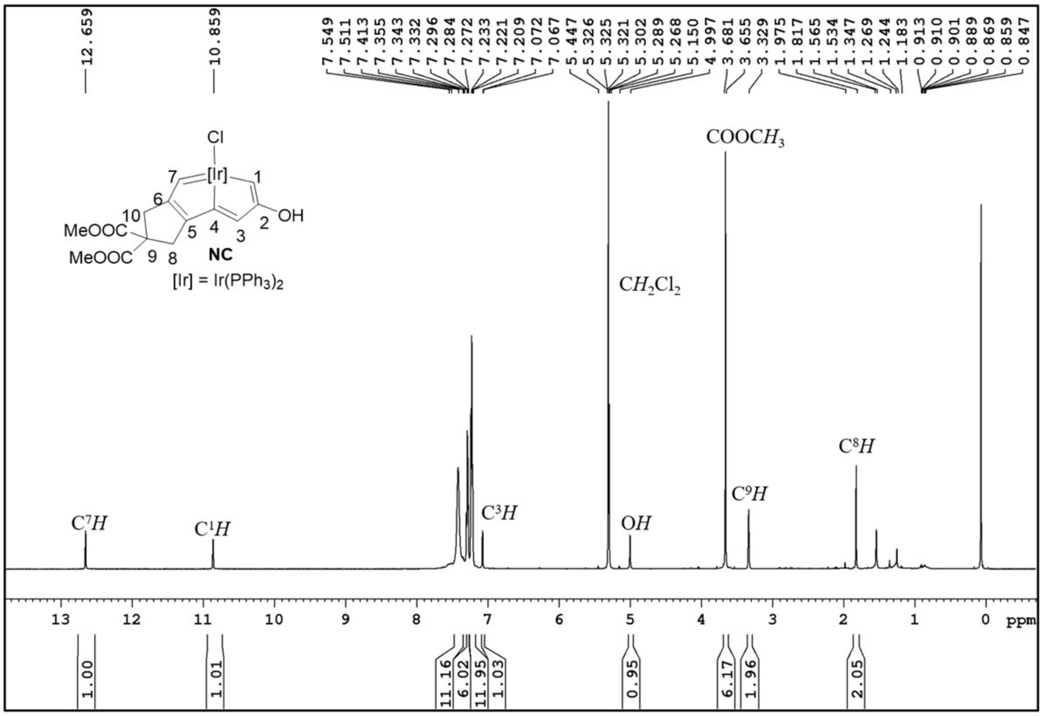

Figure S1. The ^{1}H NMR (600.0 MHz, CD_2Cl_2) spectrum of compound **NC.**

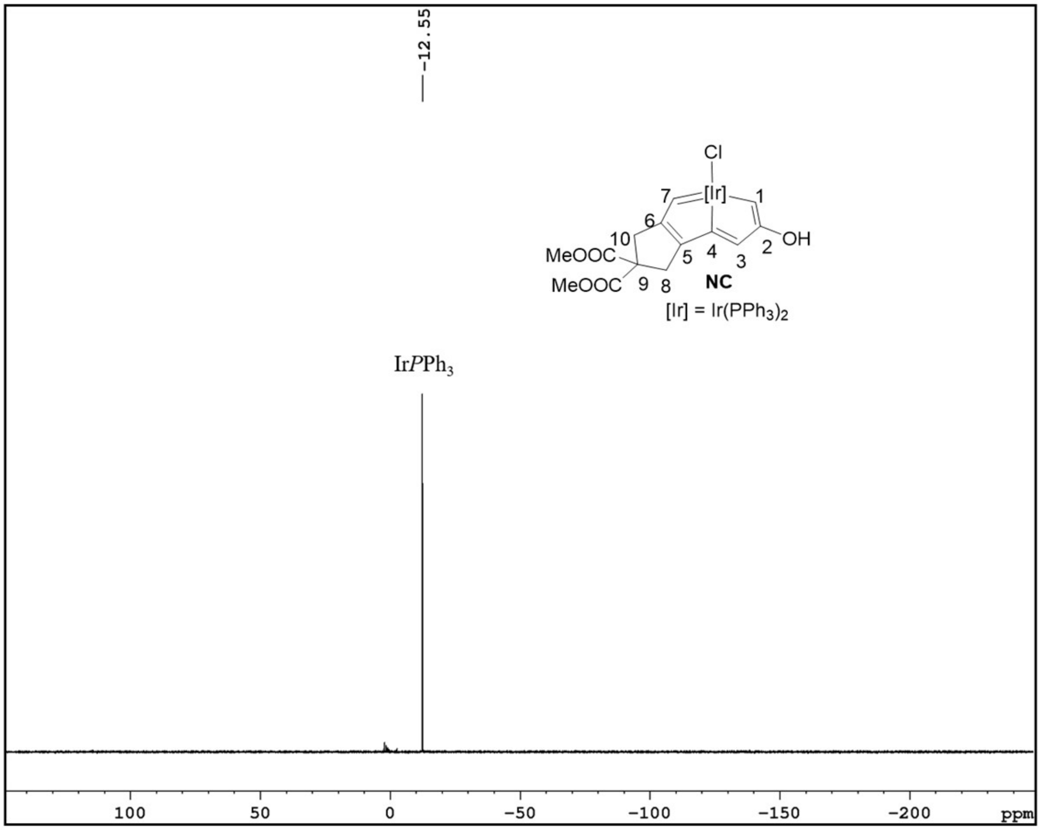

Figure S2. The $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum of compound **NC.**

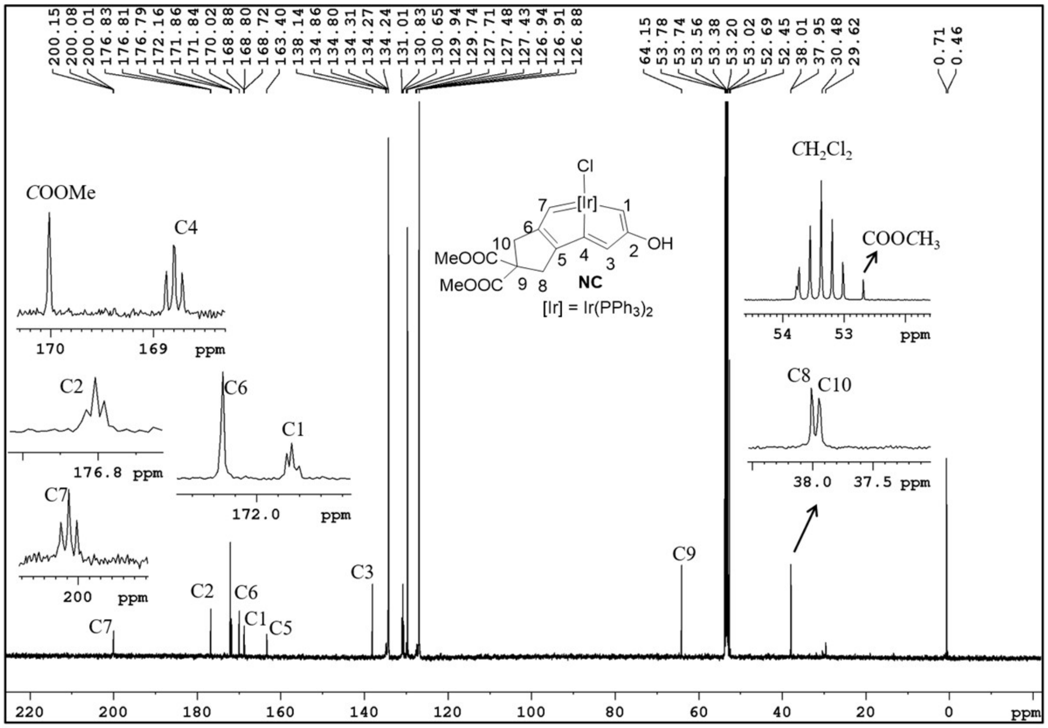

Figure S3. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum of compound **NC**.

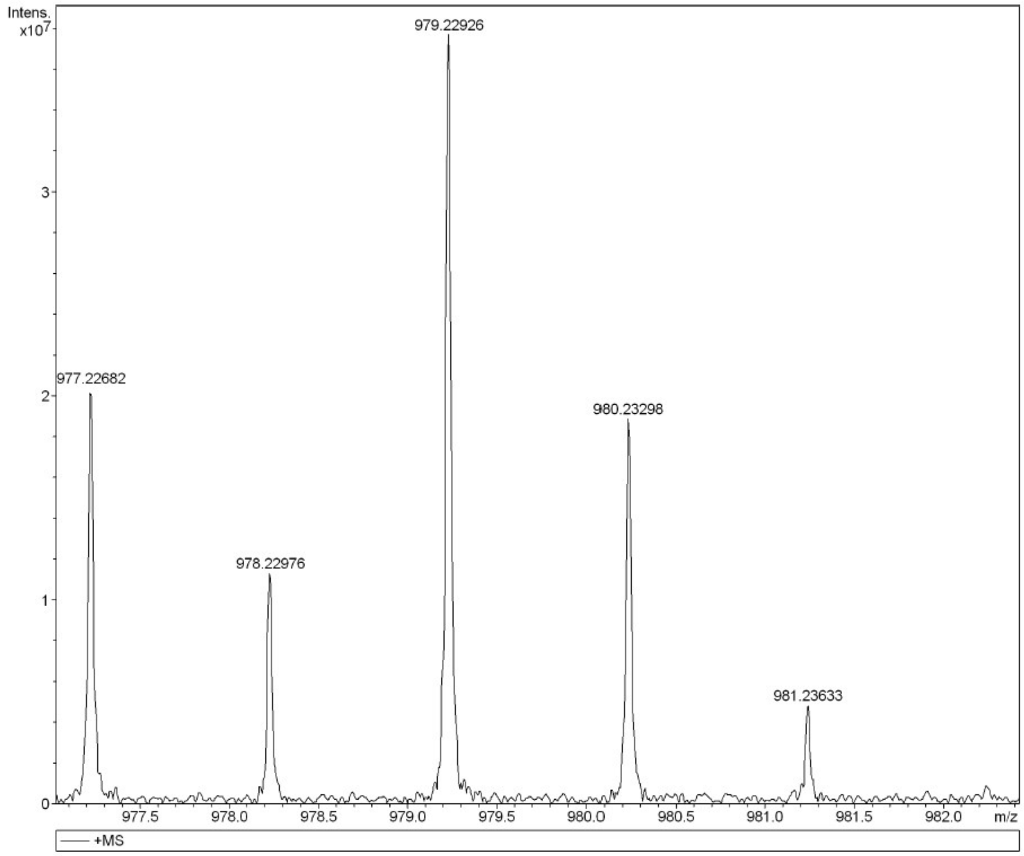

Figure S4. Positive ion ESI-MS spectrum of **[NC-Cl]**$^+$ $[C_{50}H_{44}IrO_5P_2]^+$ measured in methanol.

X-ray Crystallographic Analysis

The crystal of compound **NC** suitable for X-ray diffraction was grown from the CH_2Cl_2 solution layered with ethyl ether. Single-crystal X-ray diffraction data were collected on XtaLAB Synergy, Dualflex, HyPix Area Detector with mirror-monochromated CuKα radiation ($\lambda = 1.54184$ Å). All the Data were corrected for absorption effects using the multi-scan technique. Using Olex2[1], the structure of compound **NC** was solved with the XT[2] structure solution program using Intrinsic Phasing; the structure was refined with the ShelXL[3] refinement package using least-squares minimization. All the non-hydrogen atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were placed at their idealized positions and refined using a riding model unless otherwise stated. The atoms of COOMe groups were disordered and refined by using restraints. CCDC-2224664 (**NC**) contain the supplementary crystallographic data for this paper, and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. For further details on the crystal data, data collection, and refinements are provided in **Tables S1**.

Table S1. Crystal data and structure refinement for **NC**.

	NC·H_2O
Formula	$C_{50}H_{64}ClIrO_6P_2$
Mr	1032.46
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	18.4599(10)
b [Å]	9.2236 (10)
c [Å]	25.9361(2)
α [°]	90
β [°]	100.3000(10)
γ [°]	90
V [Å^3]	4344.89(6)
Z	4
ρ_{calcd} [gcm^{-3}]	1.578
μ [mm^{-1}]	7.618
F(000)	2072.0
Crystal size [mm^3]	0.20×0.10×0.05
Radiation (Å)	CuKα (λ = 1.54184)
θ range [°]	3.861 to 66.6
Reflns collected	30001
Independent reflns	7634
Observed reflns [$I \geq 2\sigma$]	23917
Data/restraints/params	7634/97/537
GOF on F^2	1.040
$R_1/wR_2[I \geq 2\sigma(I)]$	0.0341/0.0857
R_1/wR_2 (all data)	0.0367/0.0888
Largest peak/hole [e Å^{-3}]	2.54/-1.90

Table S2. Selected bond distances and bond angles for **NC**.

Bond Distances(Å)					
Ir1−C1	2.075(4)	C2−C3	1.409(5)	C5−C8	1.497(6)
Ir1−C4	2.011(4)	C3−C4	1.381(5)	C6−C10	1.499(6)
Ir1− C7	2.035(4)	C4−C5	1.410(5)	C8−C9	1.568(6)
Ir1− Cl1	2.5283(9)	C5−C6	1.398(6)	C9−C10	1.546(6)
C1−C2	1.394(6)	C6−C7	1.397(5)	C2−O1	1.365(5)

Bond Angels(°)			
Ir1-C1-C2	113.1(3)	C1-C2-C3	116.8(3)
Ir1-C4-C3	117.4(3)	C2-C3-C4	113.8(3)
Ir1-C4-C5	113.4(3)	C4-C5-C6	115.5(4)
Ir1-C7-C6	112.3(3)	C5-C6-C7	117.1(4)
C1-Ir1-C4	78.88(15)	C1-C2-O1	123.9(3)
C4-Ir1-C7	81.58(15)		

Calculation

The molecular optimization was calculated at th**e M06L/6-31G*** level with SDD for iridium atoms.[4, 5] The energies of their molecular orbitals were further calculated at the B3PW91/def2-TZVP level.[4, 5] The above calculations were performed in Guassian 09D.01 packages.[4, 5]

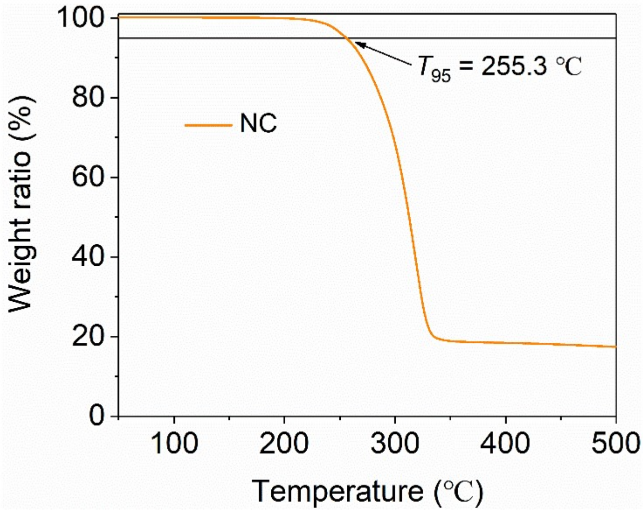

Figure S5. TGA curve of NC.

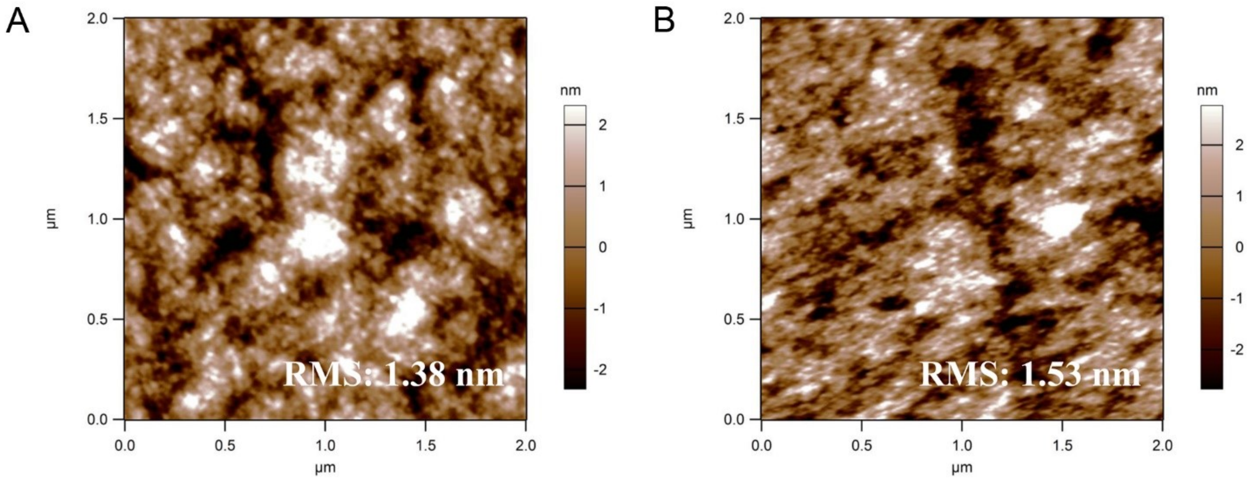

Figure S6. AFM images of NC film (8-10 nm) prepared on glass (A) before and (B) after 85 ℃ heating for 24 h.

Table S3. Photovoltaic parameters of typical PSCs based on **NC** with different processing concentrations measured by reverse scans under 1-sun illumination.

Concentrations (mg mL^{-1})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0.5	1.11	19.26	74.23	15.87
0.75	1.13	23.66	81.43	21.77
1	1.15	24.09	81.75	22.65
1.25	1.14	23.57	81.24	21.83
1.5	0.89	21.42	73.59	14.03

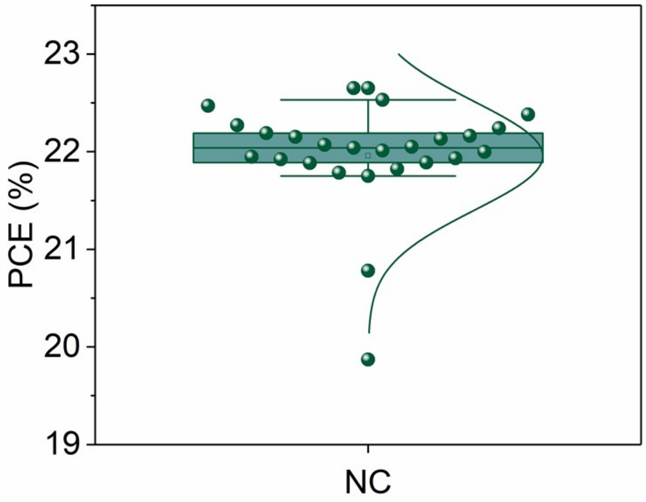

Figure S7. Statistics of device PCE based on NC.

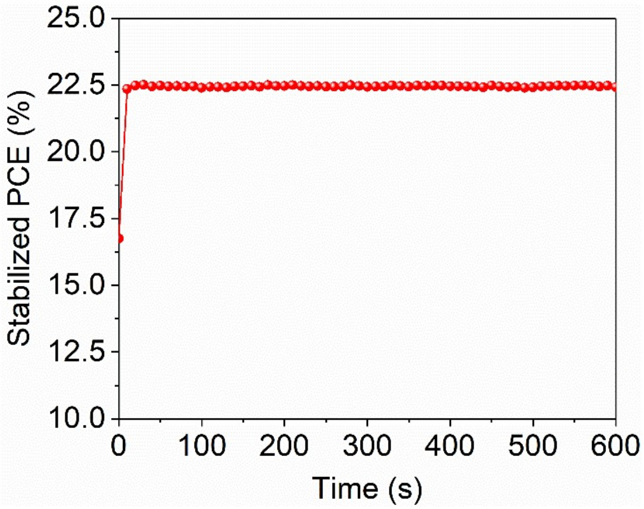

Figure S8. Stabilized PCE output based on NC.

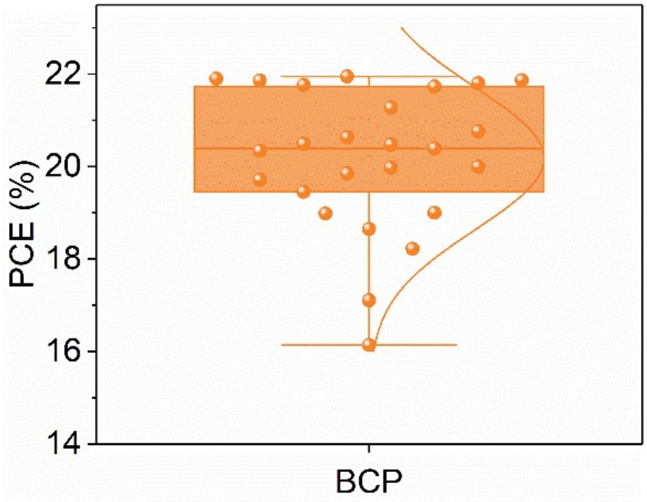

Figure S9. Statistics of device PCE based on BCP. Average PCE is 20.17 ± 1.51.

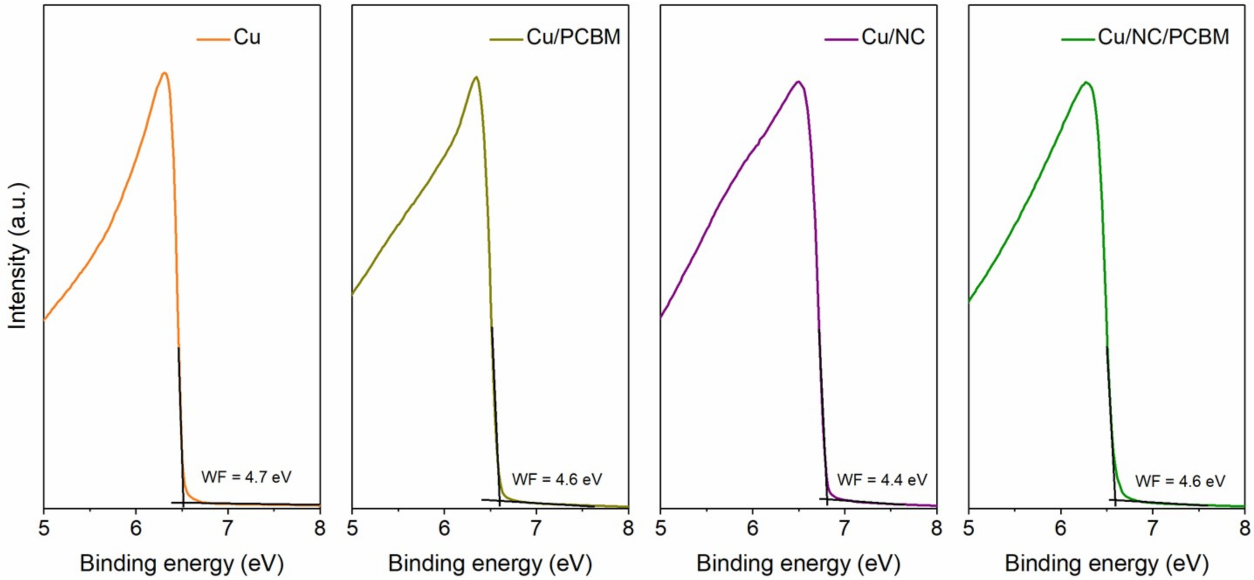

Figure S10. UPS spectra of Cu, Cu/PCBM, Cu/NC and Cu/NC/PCBM.

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