

Supporting Information

A chlorinated lactone polymer donor featuring high performance and low cost

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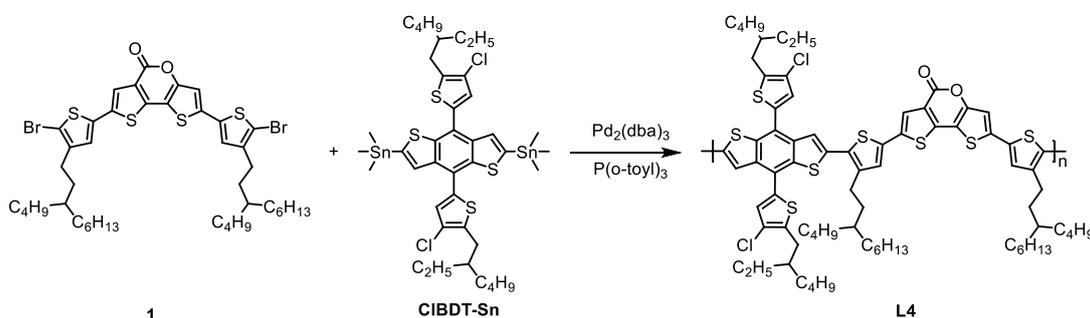
[‡] Ke Jin and Zongliang Ou contributed equally to this work.

1. General characterization

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode. L4 was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc^+ . AFM was performed on a Multimode microscope (Bruker-M8-HR) by using tapping mode.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., SunaTech Co. and other commercial suppliers. N3 was purchased from eFlexPV Co. Compound 1 was prepared according to literature.^[1] The polymerization was carried out by using standard Schlenk techniques.



Scheme S1. Synthesis of L4.

L4. To a mixture of compound 1 (100.0 mg, 0.11 mmol), CIBDT-Sn (108.8 mg, 0.11 mmol), $\text{Pd}_2(\text{dba})_3$ (3.1 mg, 0.0034 mmol) and $\text{P}(\text{o-Tol})_3$ (10.2 mg, 0.034 mmol) in a Schlenk flask was added toluene (2 mL) under argon. The mixture was heated to reflux for 16 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$ (1:1), CHCl_3 and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **L4** as a brown solid (127 mg, 83%). The M_n for L4 is 51.8 kDa, with a PDI of 1.58. ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 6.47 (br, aromatic protons), 2.89-2.86 (br, aliphatic protons), 1.54-0.67 (br, aliphatic protons).

3. NMR

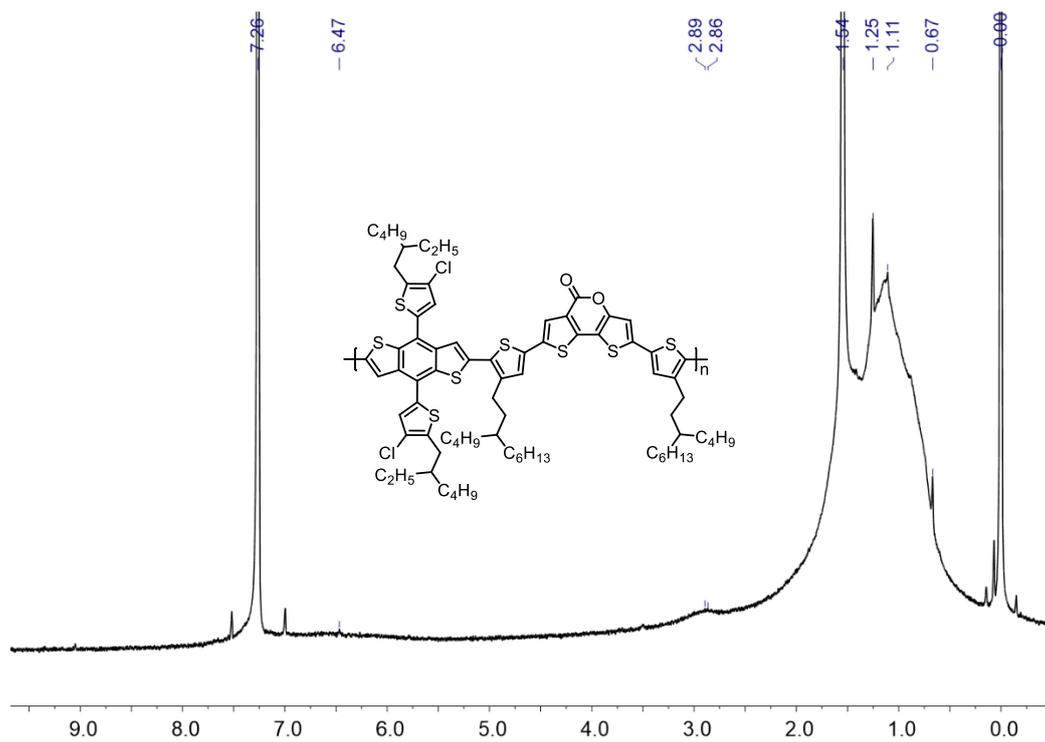


Fig. S1 ^1H NMR spectrum of L4.

4. UV-Vis

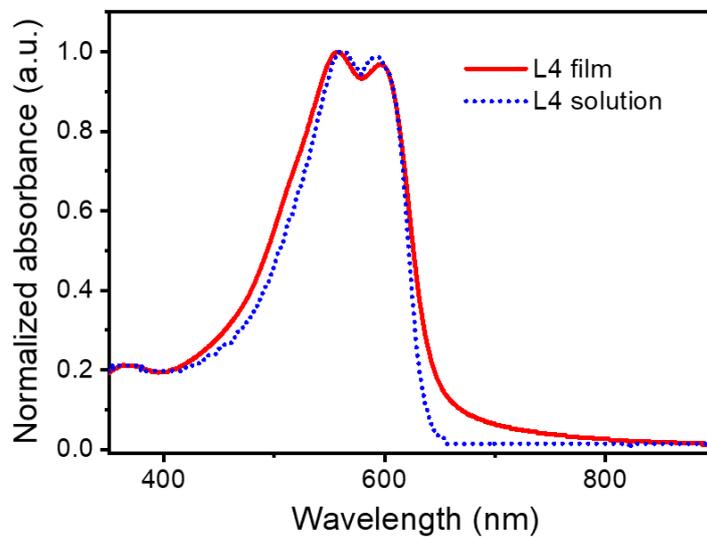


Fig. S2 Absorption spectra for L4 in chloroform and as a film.

5. CV

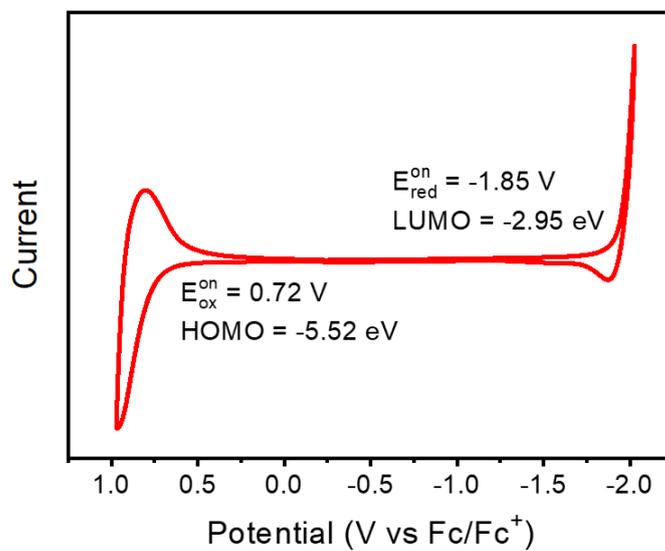


Fig. S3 Cyclic voltammogram for L4.

6. Device fabrication and measurements

Conventional solar cells

A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A L4:N3 (or L4:N3:PC₆₁BM) blend in chloroform (CF) was spin-coated onto PEDOT:PSS layer. PDIN (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Ag (~80 nm) was evaporated onto PDIN through a shadow mask (pressure ca. 10⁻⁴ Pa). The effective area for the devices is 4 mm². The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm²). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by the National Institute of Metrology (NIM). When doing *J-V* measurement, a metal mask with an aperture (2.56 mm²) was used to define the effective area. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech). The best cells were further tested at NIM for certification. A metal mask with an aperture (2.580 mm²) was used to define the effective area.

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Al. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A L4:N3 (or L4:N3:PC₆₁BM) blend in CF was spin-coated onto PEDOT:PSS layer. Finally, MoO₃ (~6 nm) and Al (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is ITO/ZnO/active layer/PDIN/Al. The ZnO precursor solution was prepared according to literature.^[2] It was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 30 min. ZnO film thickness is ~30 nm. A L4:N3 (or L4:N3:PC₆₁BM) blend in CF was spin-coated onto ZnO layer. PDIN (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Al (~100 nm) was evaporated onto the active layer through a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for L4:N3 solar cells.^a

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:1	0.845	24.43	74.3	15.33 (15.13) ^b
1:1.2	0.848	25.56	74.4	16.12 (15.91)
1:1.4	0.848	25.58	75.6	16.39 (16.25)
1:1.6	0.847	25.40	74.9	16.10 (15.97)

^aBlend solution: 13 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of the active layer thickness for L4:N3 solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
185	0.838	24.32	73.5	14.97 (14.75) ^b
150	0.843	24.59	75.1	15.58 (15.40)
126	0.845	25.67	75.4	16.35 (16.18)
110	0.848	25.58	75.6	16.39 (16.26)
98	0.846	24.85	76.7	16.12 (15.91)

^aD/A ratio: 1:1.4 (w/w); blend solution: 13 mg/mL in CF.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of DPE content for L4:N3 solar cells.^a

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.848	25.58	75.6	16.39 (16.26) ^b
0.25	0.848	26.10	76.5	16.93 (16.80)
0.5	0.844	26.43	76.9	17.16 (17.06)
0.75	0.842	26.25	75.9	16.78 (16.78)

^aD/A ratio: 1:1.4 (w/w); blend solution: 13 mg/mL in CF; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of PC₆₁BM content for L4:N3:PC₆₁BM solar cells.^a

L4:N3:PC ₆₁ BM [w/w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:1.4:0	0.844	26.43	76.9	17.16 (17.06) ^b
1:1.4:0.1	0.850	26.76	78.1	17.77 (17.65)
1:1.4:0.2	0.850	27.07	78.7	18.10 (17.98)
1:1.4:0.3	0.848	27.41	76.7	17.83 (17.69)

^aBlend solution: 13 mg/mL in CF with 0.5 vol% DPE; spin-coating: 5000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

8. NIM certification for L4:N3:PC₆₁BM solar cells

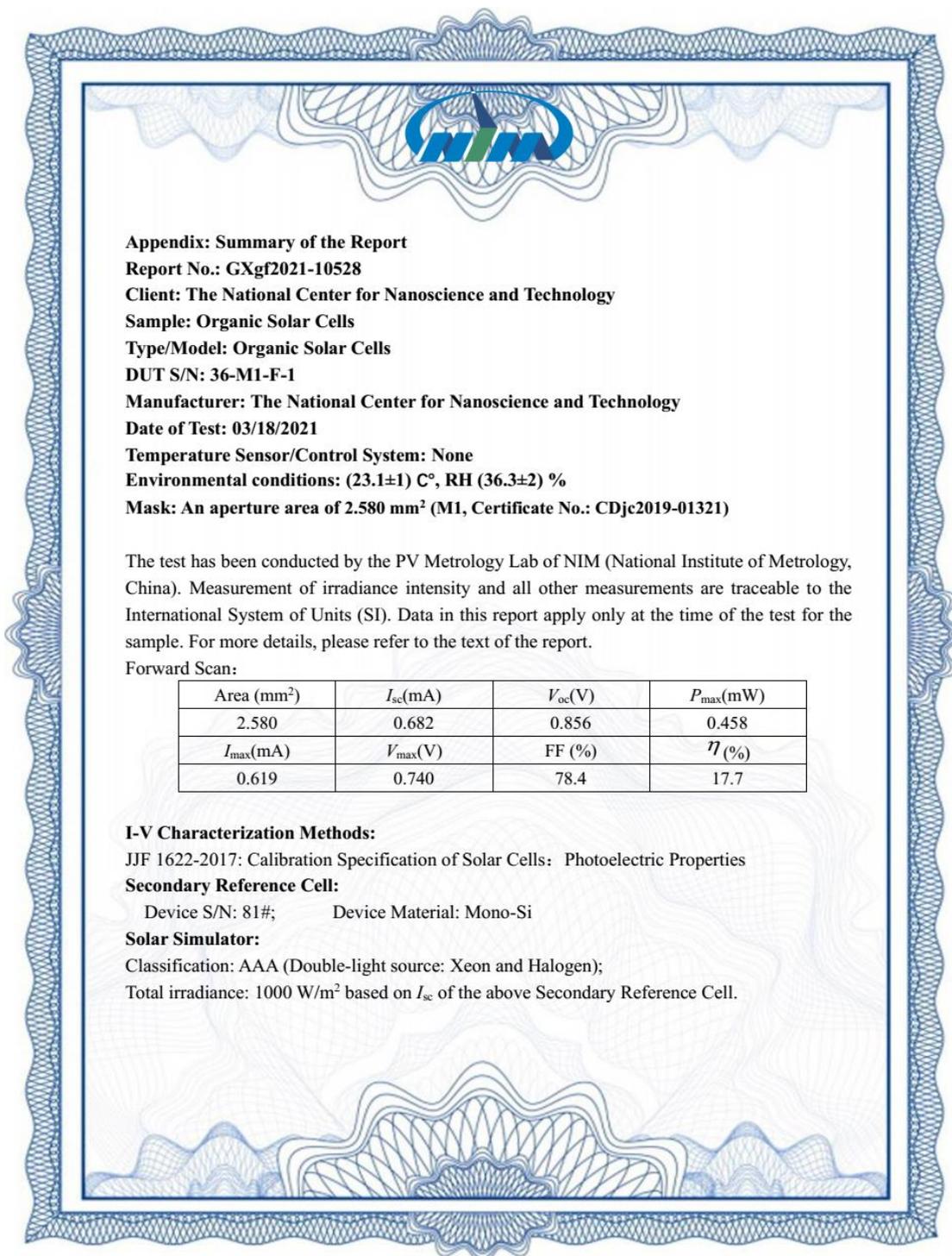


Fig. S4 NIM (Beijing) report for L4:N3:PC₆₁BM solar cells.

9. SCLC

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes, ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage ($V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, $V_{\text{bi}} = 0.1$ V for hole-only devices.^[3] The mobility was calculated from the slope of $J^{1/2}$ - V plot.

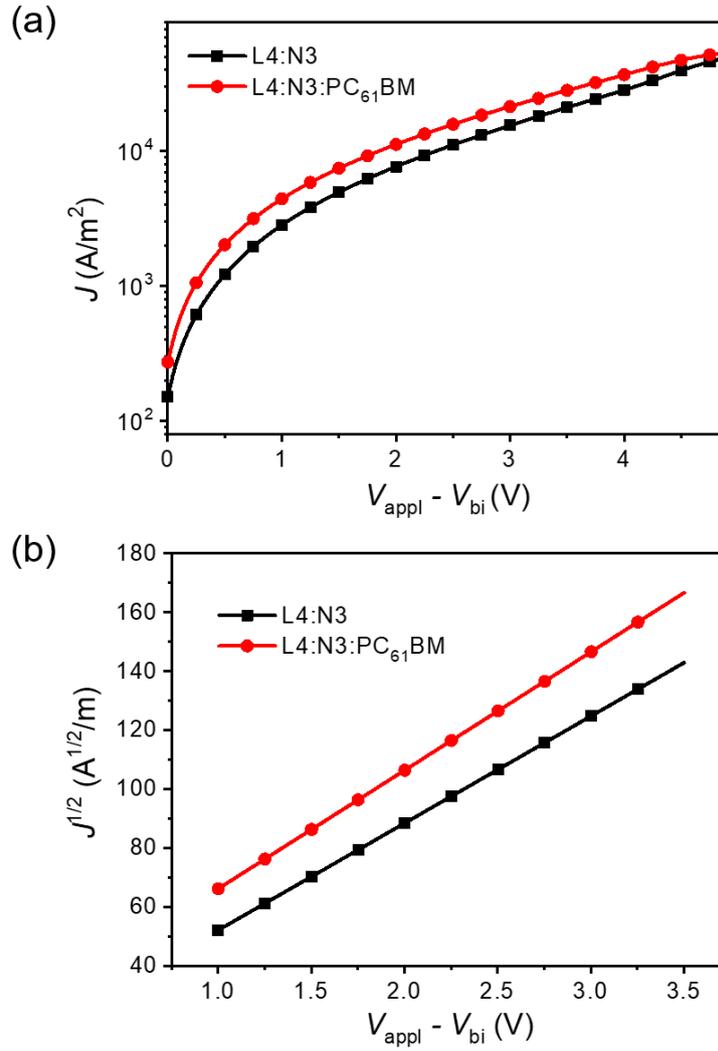


Fig. S5 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the hole-only devices (in dark). The thicknesses for L4:N3 (1:1.4) and L4:N3:PC₆₁BM (1:1.4:0.2) films are 121 nm and 119 nm, respectively.

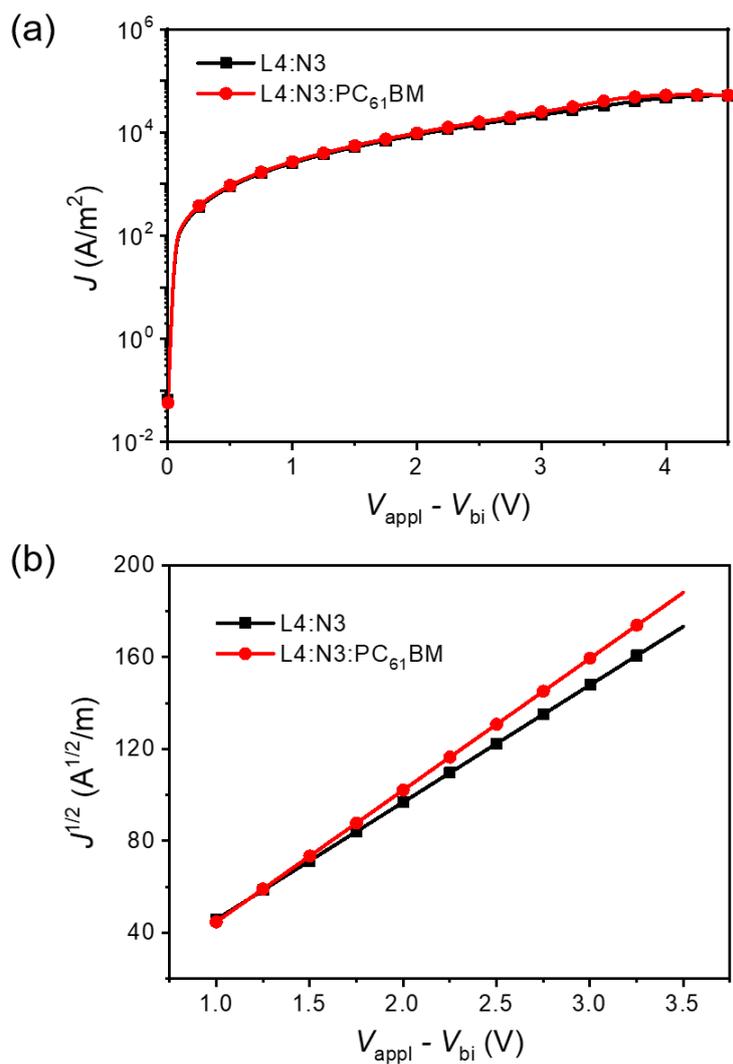


Fig. S6 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the electron-only devices (in dark). The thicknesses for L4:N3 (1:1.4) and L4:N3:PC₆₁BM (1:1.4:0.2) films are 89 nm and 92 nm, respectively.

Table S5 Hole and electron mobilities.

Blend films	μ_h	μ_e	μ_h/μ_e
	[cm ² /Vs]	[cm ² /Vs]	
L4:N3 (1:1.4)	7.91×10^{-4}	5.58×10^{-4}	1.42
L4:N3:PC ₆₁ BM (1:1.4:0.2)	9.23×10^{-4}	7.48×10^{-4}	1.23

10. AFM

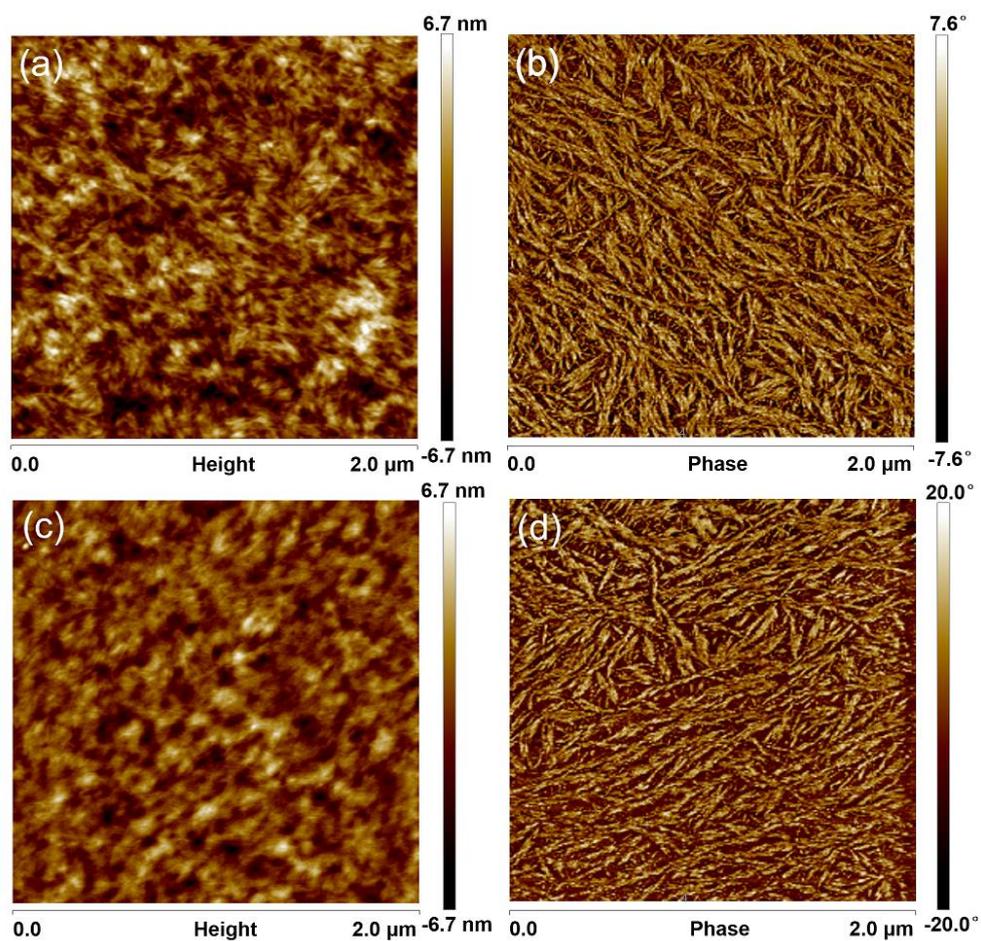


Fig. S7 AFM height (left) and phase (right) images for blend films. (a) and (b), L4:N3 ($R_{\text{rms}} = 1.88$ nm); (c) and (d), L4:N3:PC₆₁BM ($R_{\text{rms}} = 1.49$ nm). R_{rms} : root-mean-square roughness.

References

- [1] Ou Z, Qin J, Jin K, et al. Engineering of the alkyl chain branching point on a lactone polymer donor yields 17.81% efficiency. *J Mater Chem A*, 2022, DOI: 10.1039/D1TA10233H
- [2] Sun Y, Seo J H, Takacs C J, et al. Inverted polymer solar cells integrated with a lowtemperature-annealed sol-gel-derived ZnO film as an electron transport layer. *Adv Mater*, 2011, 23, 1679
- [3] Duan C, Cai W, Hsu B, et al. Toward green solvent processable photovoltaic materials for polymer solar cells: the role of highly polar pendant groups in charge carrier transport and photovoltaic behavior. *Energy Environ Sci*, 2013, 6, 3022