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Supporting Information

A large-bandgap copolymer donor for efficient ternary organic solar cells

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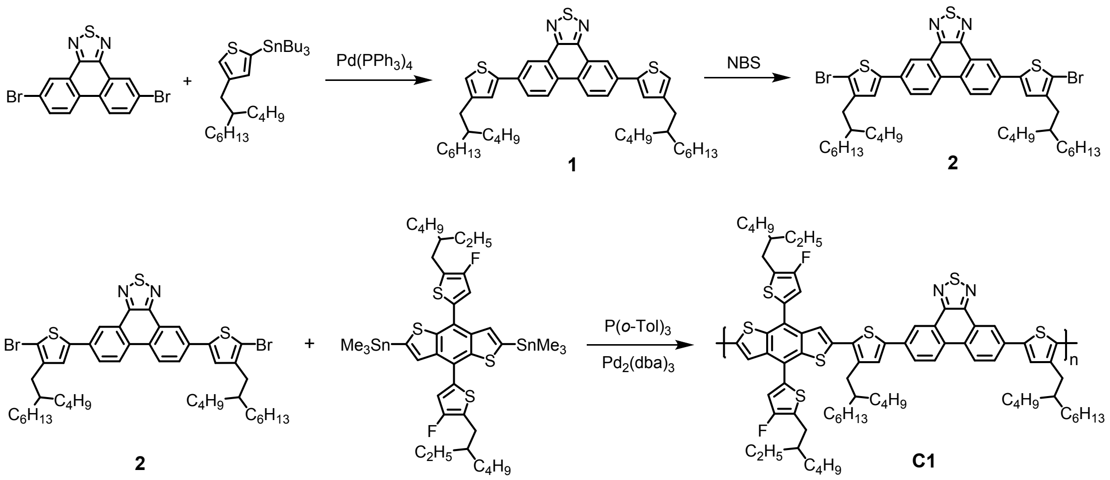
1. General characterization

^{1}H 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. The polymer was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc$^+$. AFM was performed on a Multimode microscope (Veeco) 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. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.



Scheme S1 The synthetic route for C1.

Compound 1. To a solution of 5,10-dibromophenanthro[9,10-c][1,2,5]thiadiazole (300 mg, 0.8 mmol) and tributyl(thiophen-3-yl)stannane (1.07 g, 2.0 mmol) in toluene (10mL) and DMF (2 mL) was added Pd(PPh$_3$)$_4$ (88 mg, 0.08 mmol) under N$_2$. The mixture was heated to reflux and stirred overnight. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CHCl$_3$:petroleum ether (1:3) as eluent to give **compound 1** as a yellow solid (172.4 mg, 33%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 8.77-8.75 (m, 2H), 8.29-8.27 (m, 2H), 7.85-7.85-7.82 (m, 2H), 7.34 (s, 2H), 6.94 (s, 2H), 2.60 (d, J = 6.8 Hz, 4H), 1.70 (br, 2H), 1.33-1.30 (m, 32H), 0.94-0.88 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 153.30, 143.40, 142.50, 134.18, 129.92, 126.84, 126.19, 125.87, 123.80, 121.97, 121.37, 38.92, 35.22, 33.37, 33.06, 31.94, 29.75, 28.89, 26.62, 23.10, 22.71, 14.19, 14.14. MALDI-TOF MS (m/z): $C_{46}H_{60}N_2S_3$ (M^+) calc. 736.39, found 736.64.

Compound 2. To a solution of compound 1 (65.8 mg, 0.10 mmol) in $CHCl_3$ (2.5 mL) was added NBS (36.1 mg, 0.20 mmol). The mixture was stirred for 2 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:3) as eluent to give **compound 2** as a yellow solid (55.5 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.64 (d, J = 1.8 Hz, 2H), 8.26 (d, J = 8.6 Hz, 2H), 7.74-7.71 (m, 2H), 7.16 (s, 2H), 2.53 (d, J = 7.2 Hz, 4H), 1.74 (br, 2H), 1.33-1.29 (m, 32H), 0.93-0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.15, 142.78, 142.05, 133.39, 130.04, 126.42, 126.28, 125.36, 123.94, 121.70, 110.12, 38.62, 34.42, 33.38, 33.09, 31.92, 29.74, 28.80, 26.54, 23.10, 22.70, 14.16, 14.14. MALDI-TOF MS (m/z): $C_{46}H_{59}Br_2N_2S_3$ ($M + H^+$) calc. 895.22, found 895.52.

C1. To a mixture of compound 2 (80 mg, 0.095 mmol), (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (89.7 mg, 0.095 mmol), $Pd_2(dba)_3$ (2.6 mg, 0.0029 mmol) and $P(o\text{-}tol)_3$ (8.7 mg, 0.029 mmol) in a Schlenk flask was added toluene (2 mL) under argon. The mixture was heated to reflux for 16 h. Then, 8 mL chlorobenzene was added and the mixture was stirred at 110 °C for 10 min. The solution was added into 100 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH_2Cl_2:$CHCl_3$ (1:1), $CHCl_3$, chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **C1** as a red solid (103.2 mg, 79%). The M_n for C1 is 66.9 kDa, with a PDI of 1.72. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.45 (br, aromatic protons), 2.84 (br, aliphatic protons), 1.69-0.83 (br, aliphatic protons).

3. NMR

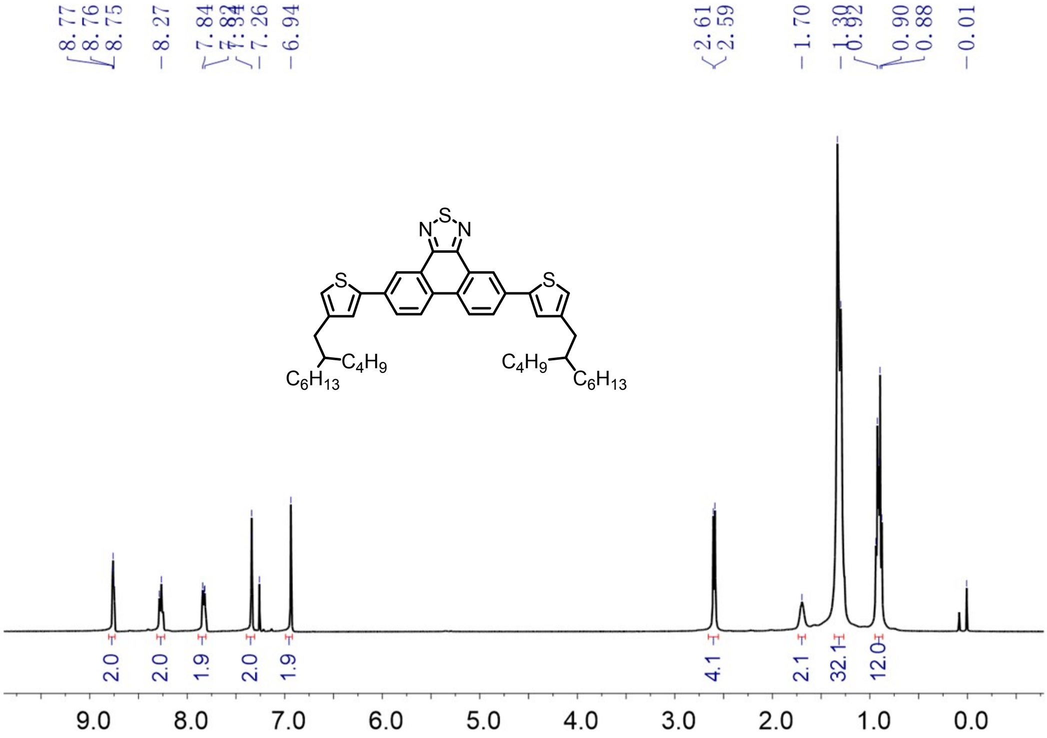


Fig. S1 ^{1}H NMR spectrum of **compound 1.**

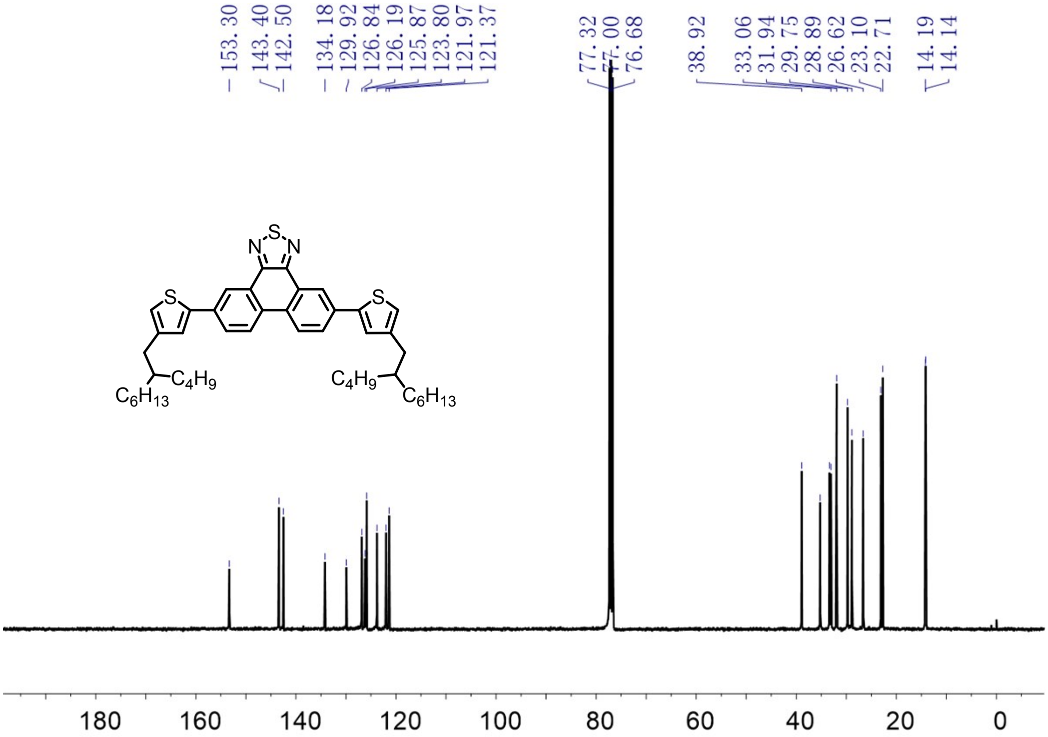


Fig. S2 ^{13}C NMR spectrum of **compound 1.**

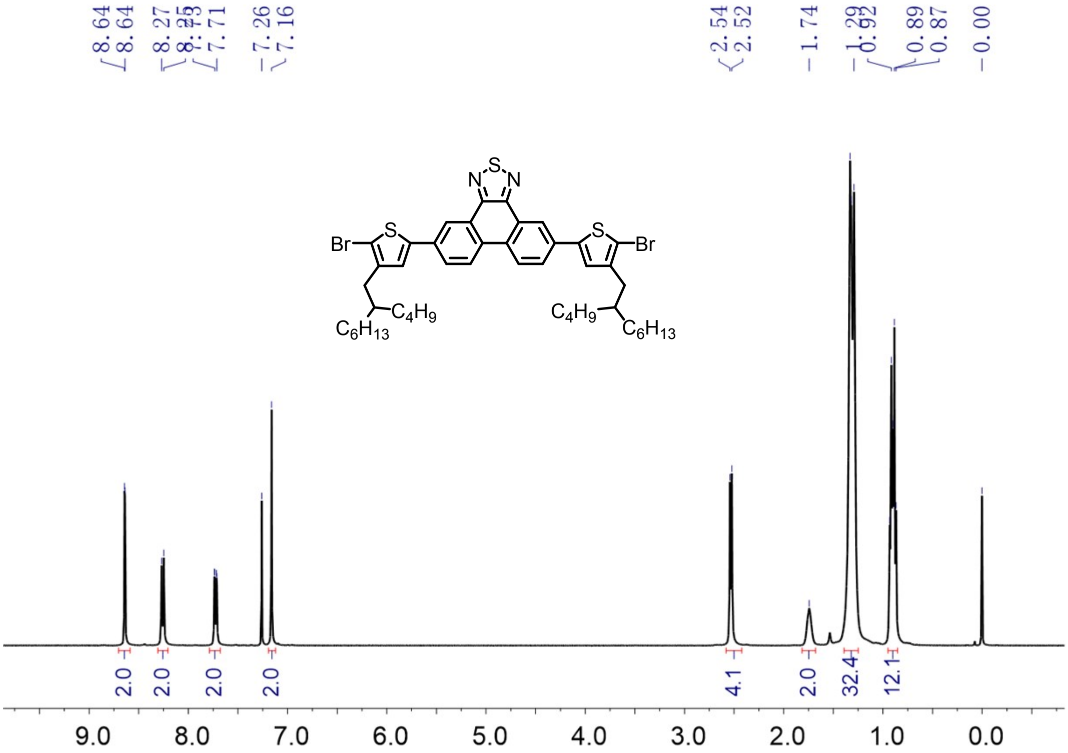


Fig. S3 ^{1}H NMR spectrum of **compound 2**.

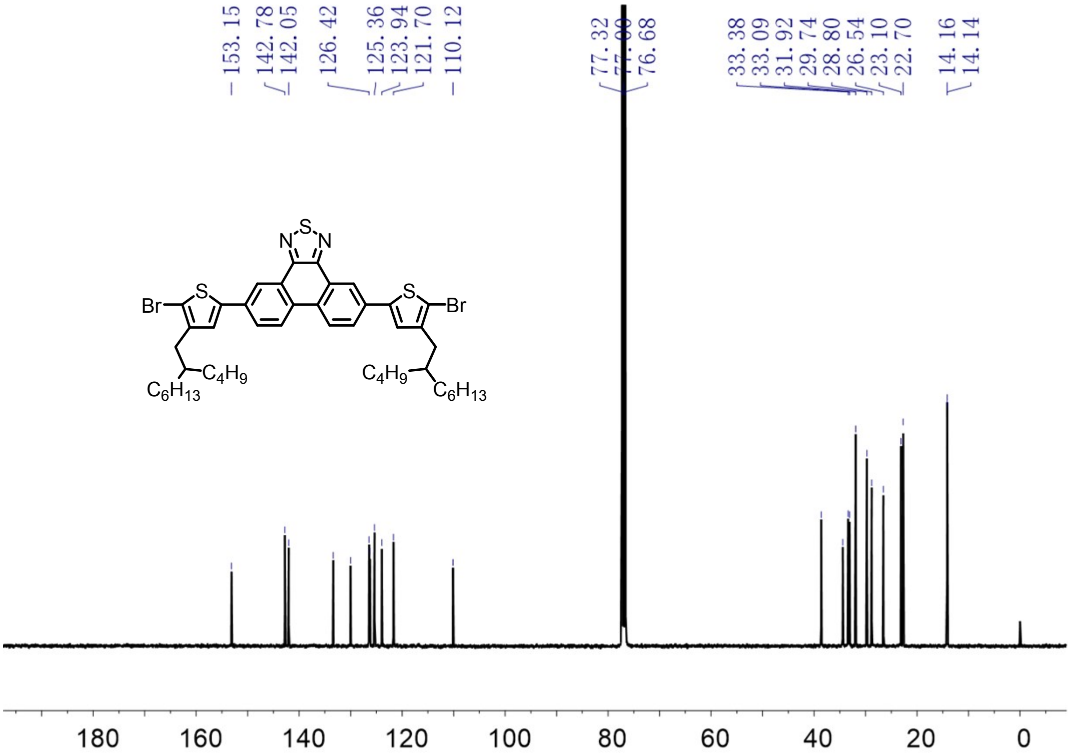


Fig. S4 ^{13}C NMR spectrum of **compound 2**.

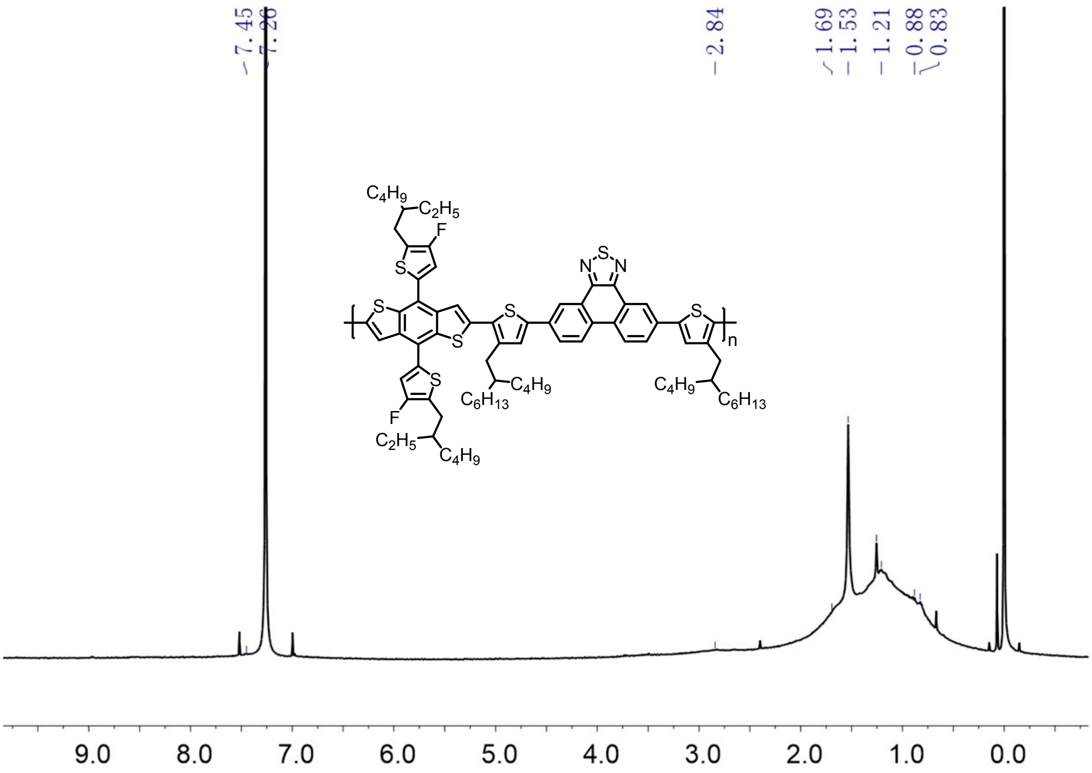


Fig. S5 ^{1}H NMR spectrum of **C1**.

4. CV

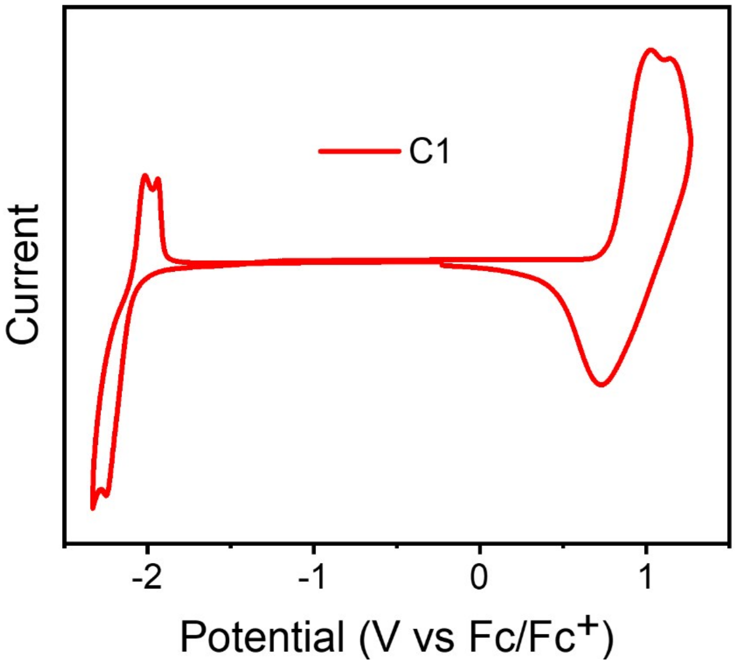


Fig. S6 Cyclic voltammogram for C1.

5. 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 L1:C1:N3 blend (14 mg/mL) in chloroform (CF) was spin-coated onto PEDOT:PSS. 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 mm^2. 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/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/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 L1:C1:N3 blend in CF was spin-coated onto PEDOT:PSS. Finally, MoO_3 (~6 nm) and Al (~100 nm) was 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 Al/active layer/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A L1:C1:N3 blend in CF was spin-coated onto Al. Ca (~5 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.

6. Optimization of device performance

Table S1 Optimization of D/A ratio for C1:N3 conventional solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.8	0.868	22.64	56.49	11.10 (10.91)[b]
1:1.2	0.859	24.19	56.30	11.70 (11.62)
1:1.4	0.866	24.66	59.53	12.72 (12.69)
1:1.6	0.864	24.00	60.73	12.60 (12.49)

[a] Blend solution: 14 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

Table S2 Optimization of active layer thickness for C1:N3 conventional solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
129	0.864	25.28	55.47	12.13 (12.02)[b]
100	0.866	24.66	59.53	12.72 (12.67)
89	0.865	20.13	64.30	11.19 (11.13)
75	0.858	16.69	67.04	9.60 (9.52)

[a] D/A ratio: 1:1.4 (w/w); blend solution: 14 mg/mL in CF.

[b] Data in parentheses are averages for 8 cells.

Table S3 Optimization of DPE content for C1:N3 conventional solar cells.[a]

DPE [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.866	24.66	59.53	12.72 (12.67)[b]
0.3	0.860	22.48	67.97	13.14 (13.02)
0.5	0.860	22.44	68.58	13.24 (13.19)
0.7	0.858	21.60	69.82	12.94 (12.77)

[a] D/A ratio: 1:1.4 (w/w); blend solution: 14 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

[b] Data in parentheses stand are averages for 8 cells.

7. EQE and absorption spectra

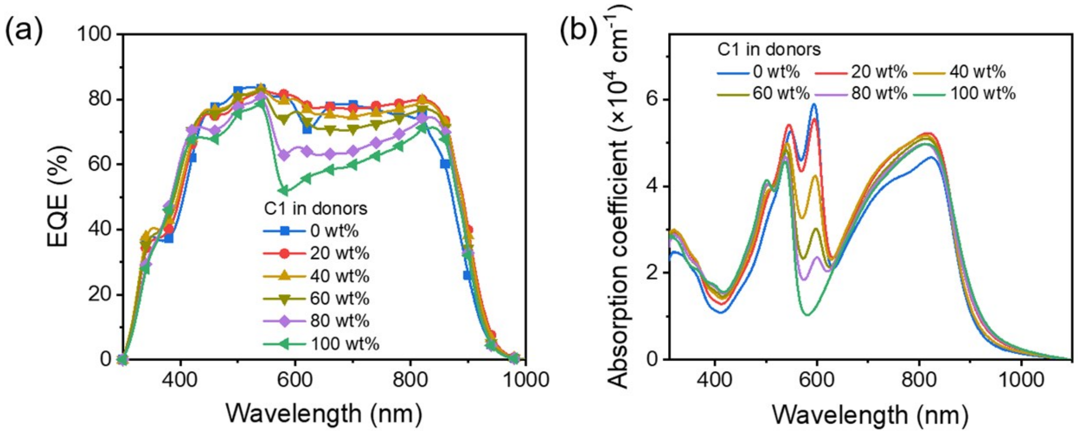


Fig. S7 (a) EQE spectra for the solar cells. (b) Absorption spectra for the blend films.

8. 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 (μ_h) or electrons (μ_e), 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 ($V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, V_{bi} = 0.1 V for hole-only devices, V_{bi} = 0 V for electron-only devices.[1] The mobility was calculated from the slope of $J^{1/2}$-V plot.

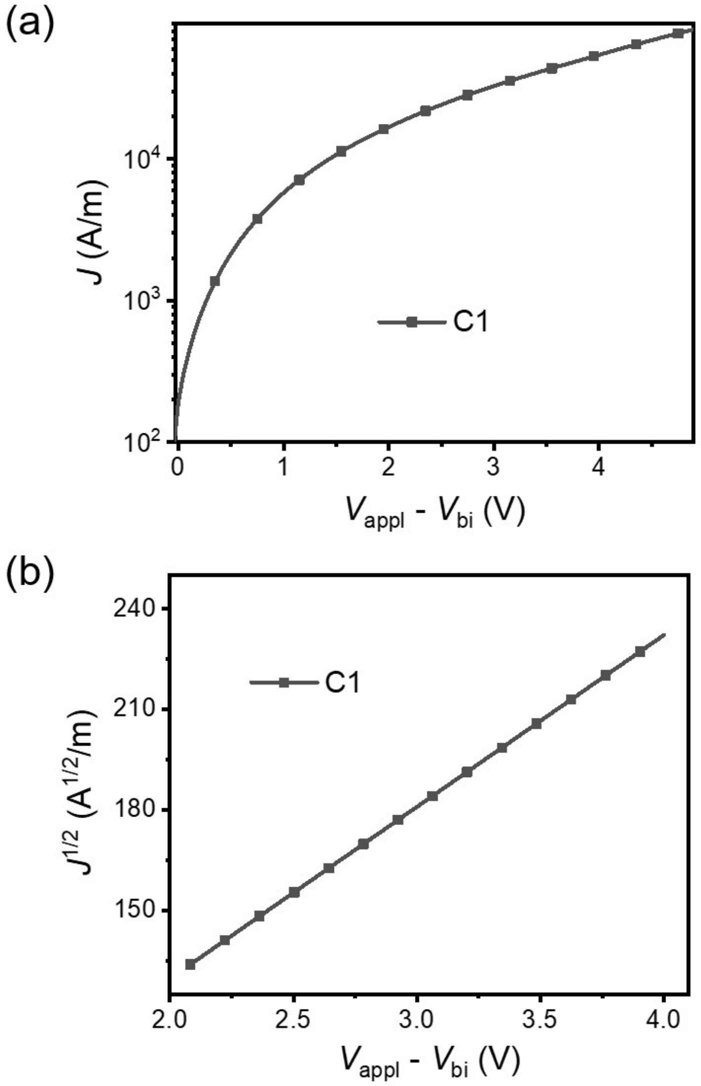


Fig. S8 *J*-*V* curve (a) and corresponding $J^{1/2}$-V plot (b) for the hole-only devices (in dark). The thickness for C1 film is 90 nm.

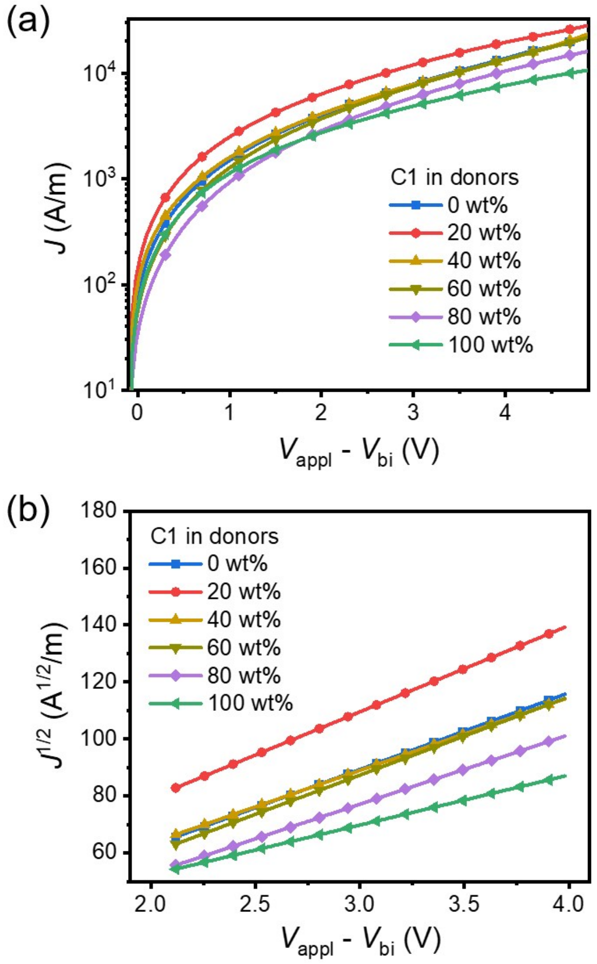


Fig. S9 *J*-*V* curves (a) and corresponding $J^{1/2}$-*V* plots (b) for the hole-only devices (in dark). The thicknesses for L1:N3 (1:1.4), L1:C1:N3 (0.8:0.2:1.4), L1:C1:N3 (0.6:0.4:1.4), L1:C1:N3 (0.4:0.6:1.4), L1:C1:N3 (0.2:0.8:1.4) and C1:N3 (1:1.4) blend films are 119 nm, 110 nm, 122 nm, 111 nm, 105 nm and 103 nm, respectively.

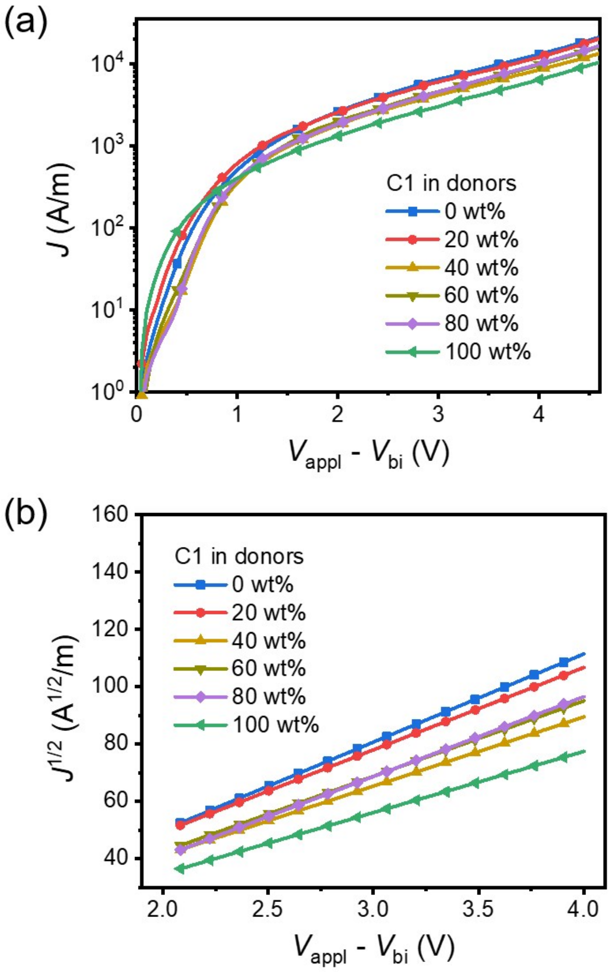


Fig. S10 *J*-*V* curves (a) and corresponding $J^{1/2}$-*V* plots (b) for the electron-only devices (in dark). The thicknesses for L1:N3 (1:1.4), L1:C1:N3 (0.8:0.2:1.4), L1:C1:N3 (0.6:0.4:1.4), L1:C1:N3 (0.4:0.6:1.4), L1:C1:N3 (0.2:0.8:1.4) and C1:N3 (1:1.4) blend films are 115 nm, 115 nm, 115 nm, 112 nm, 109 nm and 93 nm, respectively.

Table S4 Hole and electron mobilities.

Films	μ_h [cm^2/Vs]	μ_e [cm^2/Vs]	μ_h/μ_e
C1	6.44×10^{-4}	-	-
L1:N3 (1:1.4)	4.10×10^{-4}	4.82×10^{-4}	0.85
L1:C1:N3 (0.8:0.2:1.4)	4.16×10^{-4}	4.32×10^{-4}	0.96
L1:C1:N3 (0.6:0.4:1.4)	3.86×10^{-4}	3.01×10^{-4}	1.28
L1:C1:N3 (0.4:0.6:1.4)	3.45×10^{-4}	2.94×10^{-4}	1.17
L1:C1:N3 (0.2:0.8:1.4)	2.32×10^{-4}	2.80×10^{-4}	0.83
C1:N3 (1:1.4)	1.14×10^{-4}	9.09×10^{-5}	1.25

9. Bimolecular recombination

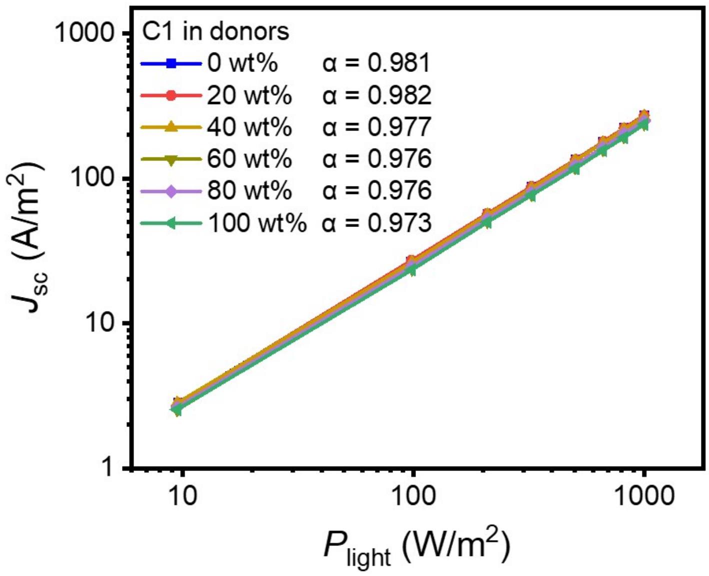


Fig. S11 J_{sc}-P_{light} plots.

10. PL

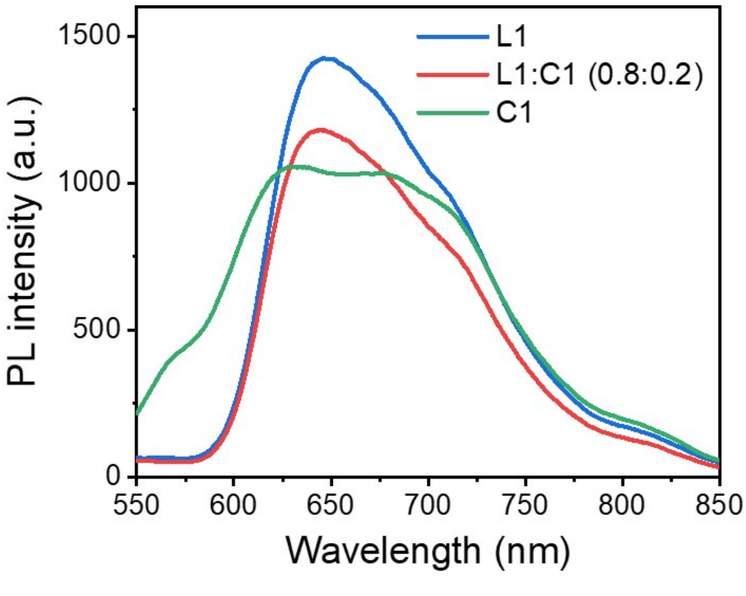


Fig. S12 PL spectra for L1, L1:C1 (0.8:0.2) and C1 films.

11. L1, L1:C1 (0.8:0.2) and C1 solar cells

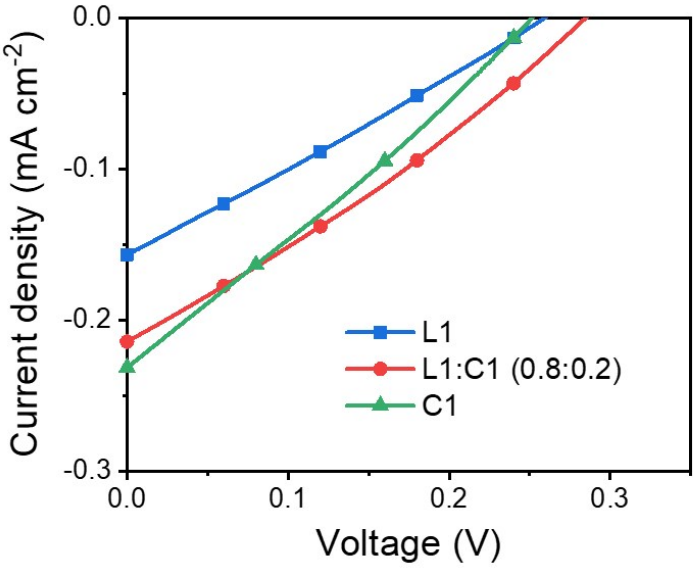


Fig. S13 *J-V* curves for L1, L1:C1 (0.8:0.2) and C1 solar cells.

12. Surface free energy measurements

The experiments were performed on a Powereach JC2000C2 contact angle goniometer. Droplets of two different liquids, water and ethylene glycol (EG) were cast onto the films with the drop size of 2 μL. Contact angle images were taken at 1 s after the whole droplet was deposited onto the sample surface. The surface free energy of each sample was calculated by:

$$\gamma_{water}(\cos\theta_{water} + 1) = 2(\gamma_{sample}{}^{d}\times\gamma_{water}{}^{d})^{1/2} + 2(\gamma_{sample}{}^{p}\times\gamma_{water}{}^{p})^{1/2}$$

$$\gamma_{EG}(\cos\theta_{EG} + 1) = 2(\gamma_{sample}{}^{d}\times\gamma_{EG}{}^{d})^{1/2} + 2(\gamma_{sample}{}^{p}\times\gamma_{EG}{}^{p})^{1/2}$$

$$\gamma_{sample}{}^{total} = \gamma_{sample}{}^{d} + \gamma_{sample}{}^{p}$$

where θ is the droplet contact angle on the sample film; $\gamma_{sample}{}^{total}$ is the surface free energy of the sample, which is equal to the sum of the dispersion ($\gamma_{sample}{}^{d}$) and polarity ($\gamma_{sample}{}^{p}$) components; γ_{water} = 72.8 mJ/m^2, $\gamma_{water}{}^{d}$ = 21.8 mJ/m^2, $\gamma_{water}{}^{p}$ = 51.0 mJ/m^2, γ_{EG} = 48.0 mJ/m^2, $\gamma_{EG}{}^{d}$ = 29.0 mJ/m^2, $\gamma_{EG}{}^{p}$ = 19.0 mJ/m^2.[2,3]

Table S5 The contact angles and surface free energy parameters.

Film	Contact Angle (°)		$\gamma_{sample}{}^{d}$	$\gamma_{sample}{}^{p}$	$\gamma_{sample}{}^{total}$
	Water	Ethylene glycol	[mJ/m^2]	[mJ/m^2]	[mJ/m^2]
L1	105.32	83.16	17.19	1.08	18.27
C1	113.42	83.45	17.04	0.14	17.18
N3	93.34	81.33	6.97	9.45	16.42

References

[1] C. Duan, W. Cai, B. B. Y. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan, A. J. Heeger and Y. Cao, 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.

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