A low-cost and green-solvent-processable hole-transport material enabled by a traditional bidentate ligand for highly efficient inverted perovskite solar cells

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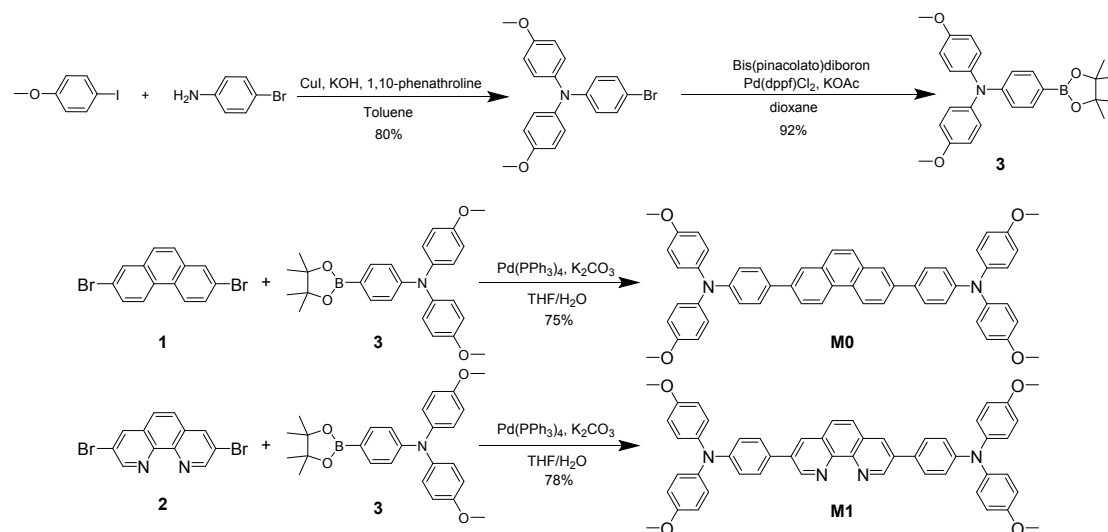[e] *School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China*

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Experimental Section

Scheme S1 Overall synthetic route of M0 and M1

M0. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 8.7 Hz, 2H), 8.03 (d, *J* = 1.8 Hz, 2H), 7.87 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.77 (s, 2H), 7.60 (d, *J* = 8.7 Hz, 4H), 7.12 (d, *J* = 8.8 Hz, 4H), 7.05 (d, *J* = 8.6 Hz, 8H), 6.86 (d, *J* = 9.0 Hz, 8H), 3.82 (s, 12H; CH$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.94, 140.89, 138.70, 132.36, 128.85, 127.72, 127.46, 126.68, 125.62, 125.47, 123.15, 120.85, 114.76, 55.54. HRMS: C$_{52}$H$_{44}$N$_2$O$_4$ calcd: 784.3296, found: 783.3294.

M1. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.40 (d, *J* = 2.3 Hz, 2H), 8.31 (d, *J* = 2.3 Hz, 2H), 7.83 (s, 2H), 7.61 (d, *J* = 8.7 Hz, 4H), 7.13 (d, *J* = 8.9 Hz, 8H), 7.07 (d, *J* = 8.7 Hz, 4H), 6.88 (d, *J* = 9.0 Hz, 8H), 3.82 (s, 12H; CH$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.01, 148.96, 140.28, 135.00, 131.82, 128.66, 128.20, 127.73, 126.75, 126.71, 120.24, 114.62, 55.32. HRMS: C$_{52}$H$_{42}$N$_4$O$_4$ calcd: 786.3206, found: 786.3203.
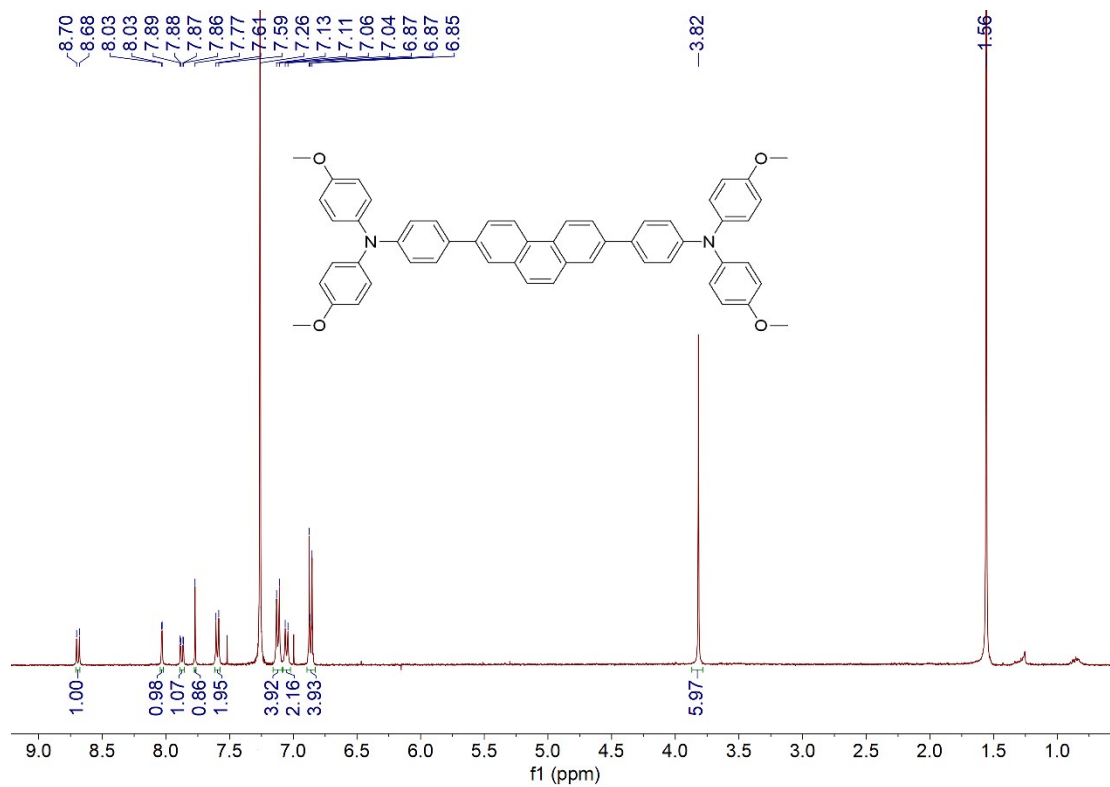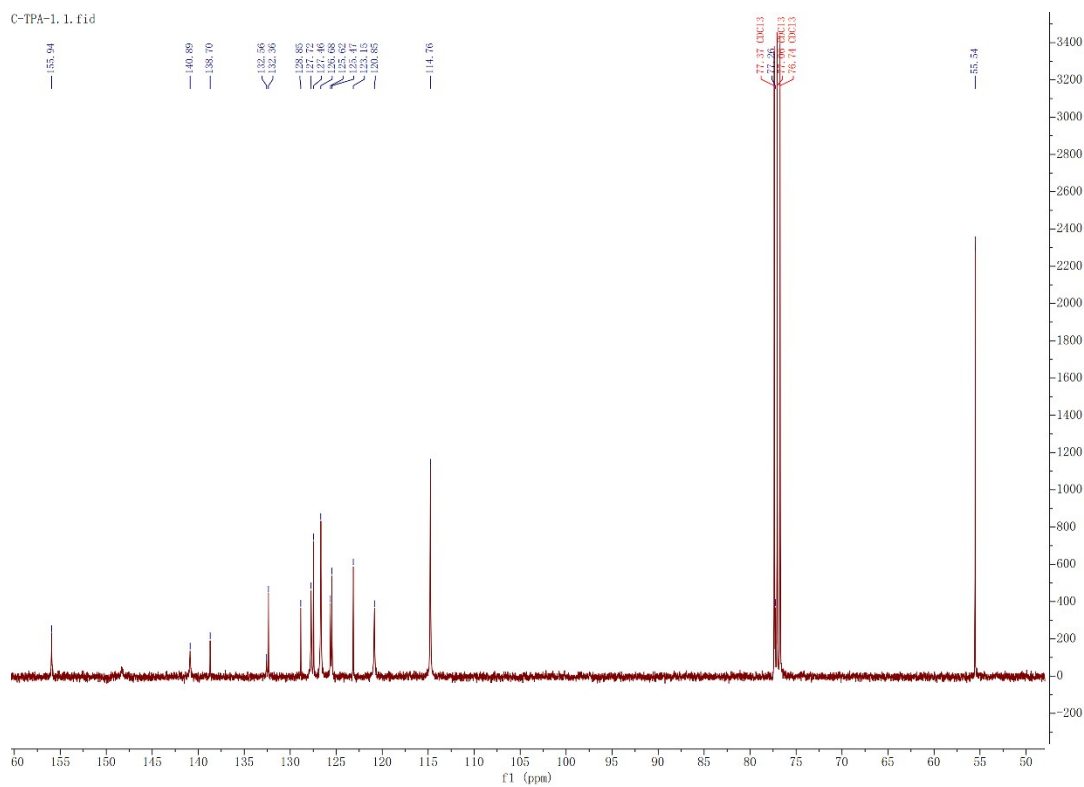
Fig. S1   ¹H NMR spectrum of **M0**.

Fig. S2   ¹³C NMR spectrum of **M0**.

Positive mode

1 #14   RT: 0.10   AV: 1   NL: 1.49E7
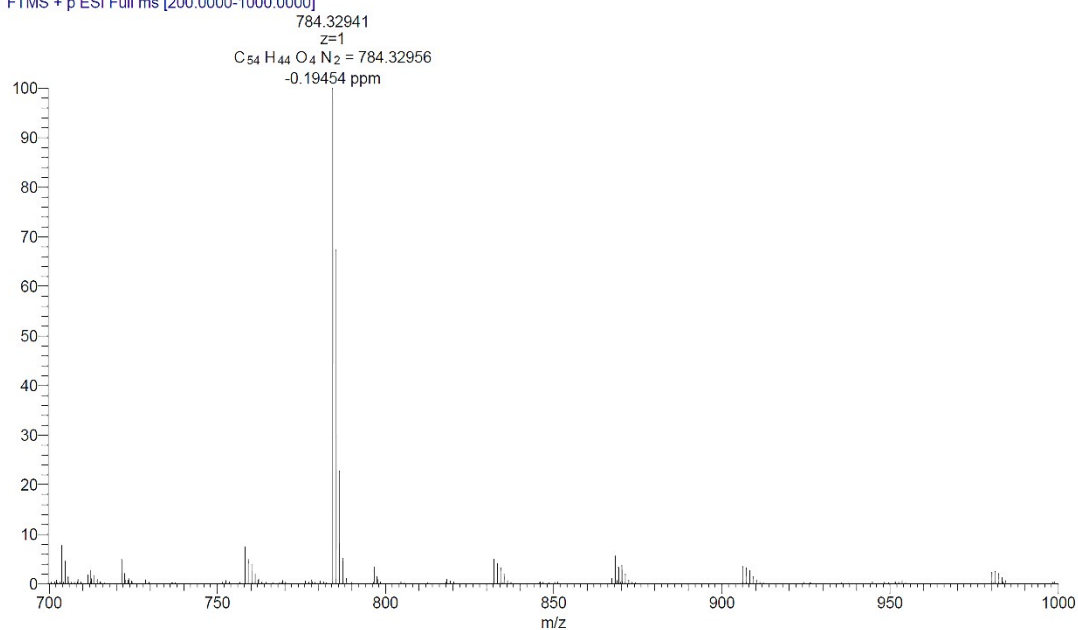T: FTMS + p ESI Full ms [200.0000-1000.0000]

784.32941
z=1
$C_{54} H_{44} O_4 N_2$ = 784.32956
-0.19454 ppm

. **Fig. S3**   HRMS of **M0**.
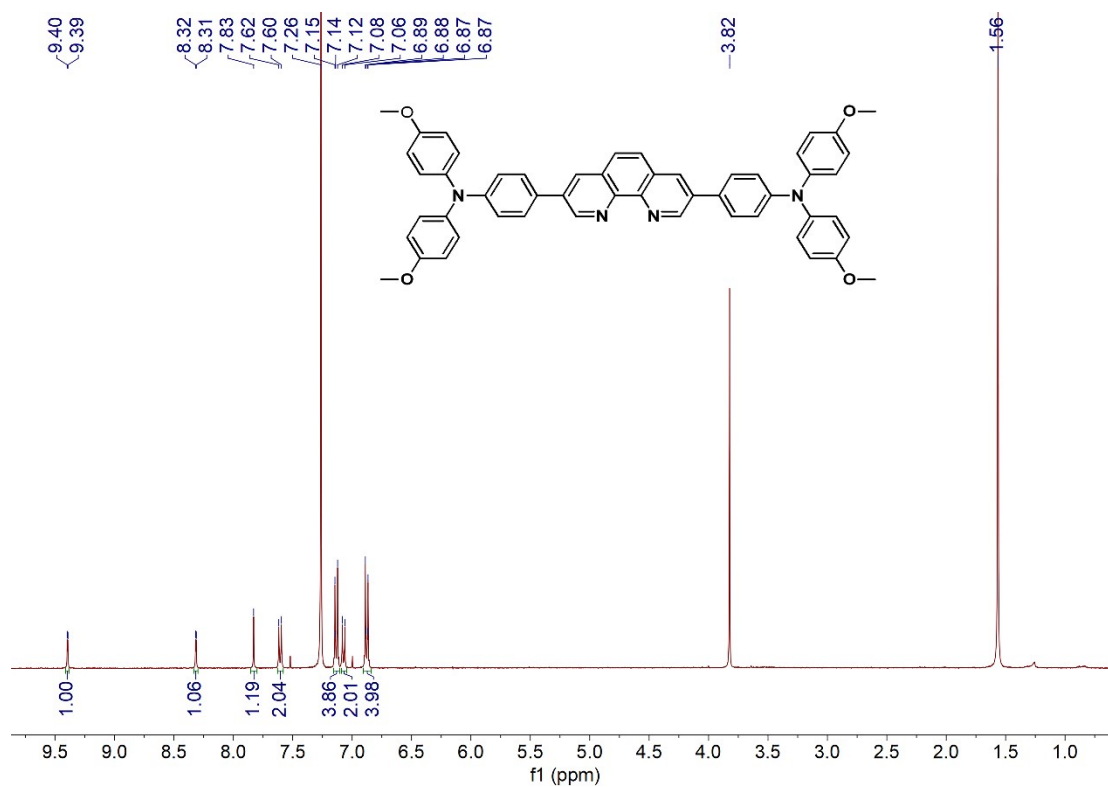
Fig. S4   ¹H NMR spectrum of **M1**.

N-TPA-1.1.fid

156.01
148.96
140.28
135.00
131.82
128.66
128.20
127.73
126.75
126.71
120.24
114.62
77.15 CDCl3
76.83 CDCl3
76.52 CDCl3
55.32
55.30
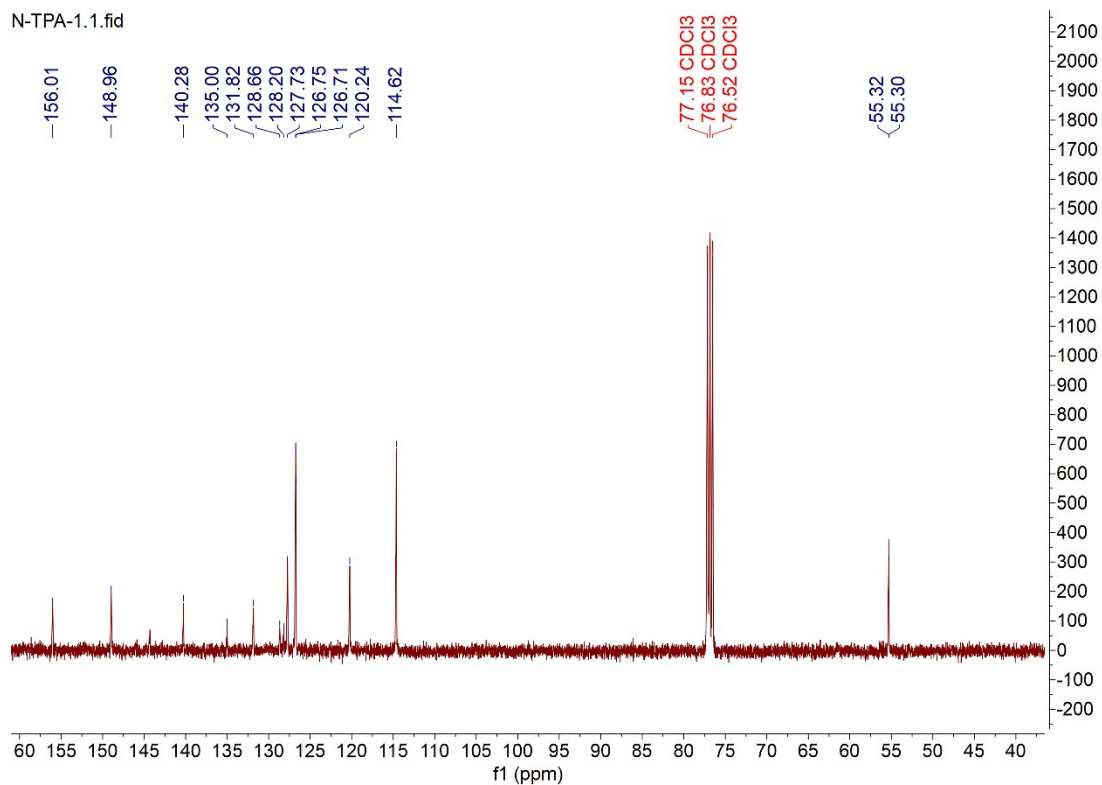
Fig. S5 ^{13}C NMR spectrum of **M1**.

Positive mode   [M+H]$^+$

2 #16 RT: 0.11 AV: 1 NL: 1.35E8
T: FTMS + p ESI Full ms [200.0000-1000.0000]

787.32819
z=1
C$_{52}$ H$_{43}$ O$_4$ N$_4$ = 787.32788
0.38579 ppm
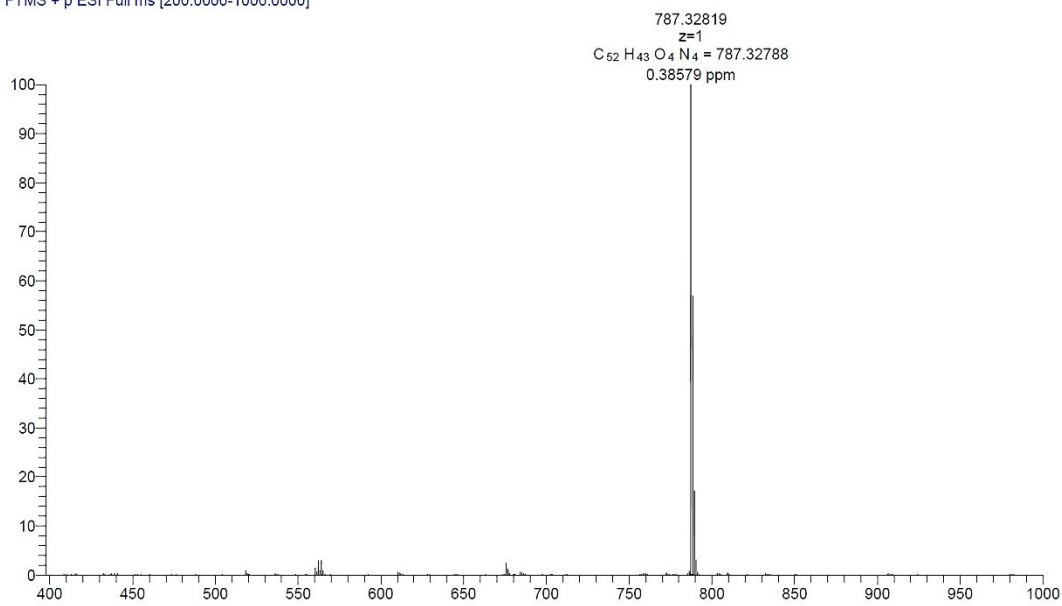
Fig. S6 HRMS of **M1**.

Table S1 Detailed calculation of cost for the synthesis of 1 g of M1

☐	Commercially available chemicals	Price	Dosage	Cost/CNY
Step 1	4-bromoaniline	500 g/130 CNY	1.36 g	0.34
	p-iodoanisole	500 g/826 CNY	4.59 g	7.48
	CuI	25 g/35 CNY	44.2 mg	0.05
	1,10-phenanthroline	100 g/210 CNY	42.5 mg	0.09
	KOH	500 g/18 CNY	3.4 g	0.12
	toluene	500 mL/30 CNY	68 mL	4.08
	petroleum ether	500 mL/12 CNY	850 mL	20.40
	CH_2Cl_2	500 mL/12 CNY	850 mL	20.40
	silica gel	500 g/15 CNY	340 g	10.20
Step 2	bis(pinacolato)diboron	500 g/900 CNY	1.87 g	3.37
	Pd(dppf)Cl_2	10 g/800 CNY	170 mg	13.60
	KOAc	500 g/40 CNY	1479 mg	0.12
	dioxane	1000 mL/200 CNY	42.5 mL	8.50
	petroleum ether	500 mL/12 CNY	850 mL	20.40
	CH_2Cl_2	500 mL/12 CNY	850 mL	20.40
	silica gel	500 g/15 CNY	340 g	10.20
Step 3	3,8-Dibromo-1,10-phenanthroline	25 g/4128 CNY	0.6 g	99.1
	Pd(PPh$_3$)$_4$	10 g/530 CNY	212.5 mg	11.22
	K_2CO_3	500 g/20 CNY	765 mg	0.03
	THF	500 mL/20 CNY	57 mL	2.27
	petroleum ether	500 mL/12 CNY	700 mL	17.04
	CH_2Cl_2	500 mL/12 CNY	70 mL	17.04
	silica gel	500 g/15 CNY	283 g	8.52
total cost	☐	☐		295
				(45 US$)

Table S2. Solubility test of M0 and M1 in chlorobenzene or ethyl acetate at room temperature

HTM	Chlorobenzene (mg mL^{-1})	Ethyl acetate (mg mL^{-1})
M0	~45	~5
M1	~22	~0.9
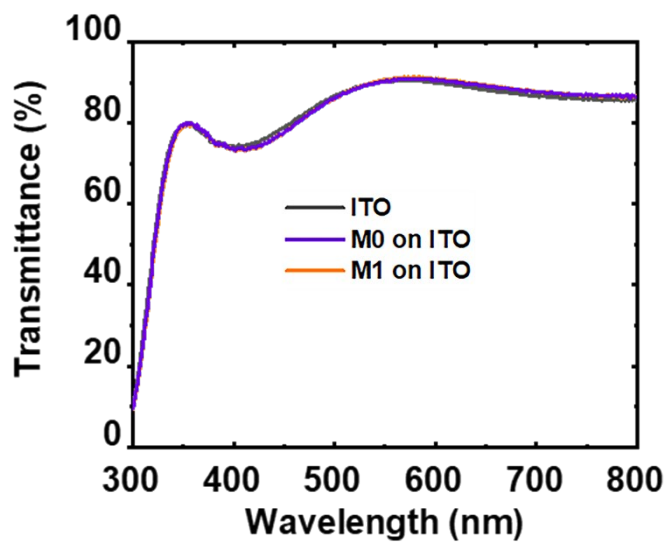
Fig. S7 Transmittance spectroscopy for the pure ITO (black line), M0 on ITO, and M1 on ITO.
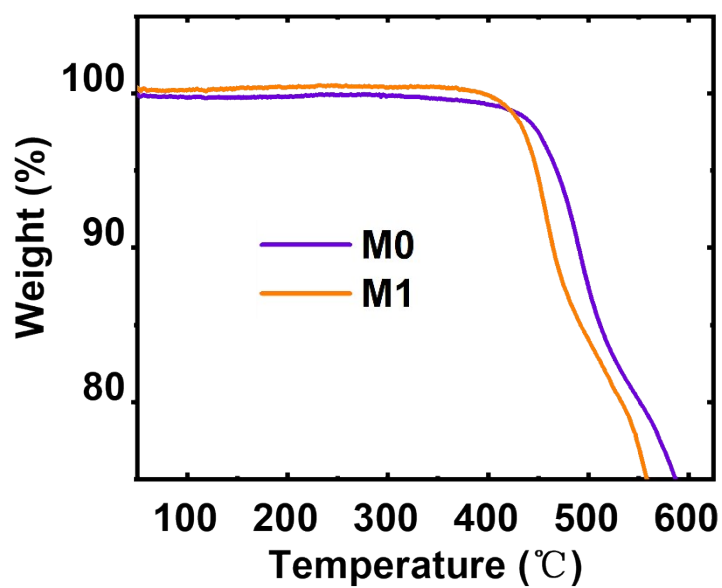

Fig. S8 TGA curves of M0 and M1 which was measured at a heat ramp of 10 °C min^{-1}

SCLC Mobility measurement

Hole and electron mobilities were characterized using the space-charge-limited current (SCLC) method. The device structure of ITO/PEDOT:PSS/HTM/Au was used for hole-only devices. The SCLC mobilities were calculated using the MOTT-Gurney equation:

$$J = 9/8\ \varepsilon_0\ \varepsilon_r\ \mu\ V^2/d^3$$

where J is the current density, ε_r is the relative dielectric constant of the active layer, herein, we use a relative dielectric constant of 3 for the polymer. ε_0 is the permittivity of empty space, μ is the mobility of hole or electron, and d is the thickness of the active layer, V is the internal voltage in the device, and $V = V_{appl} - V_{bi}$, where V_{appl} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (in the hole-only and the electron-only devices, the V_{bi} values can be neglected).
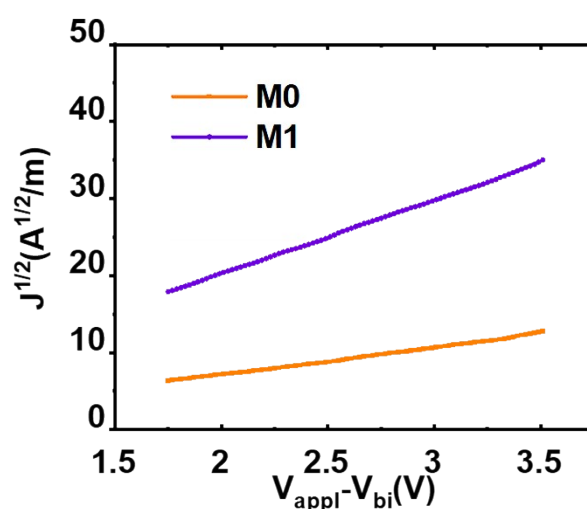
Fig. S9 The corresponding $J^{1/2}$-V curves for the hole-only devices are based on the pure HTM films with a device structure of ITO/PEDOT:PSS/HTM/Au.
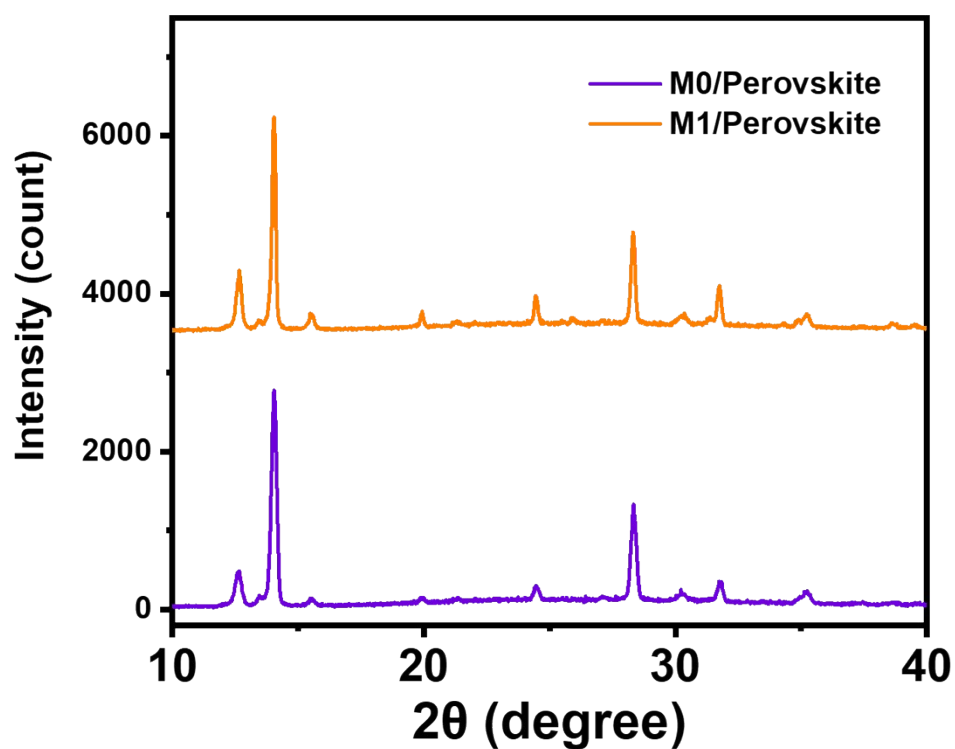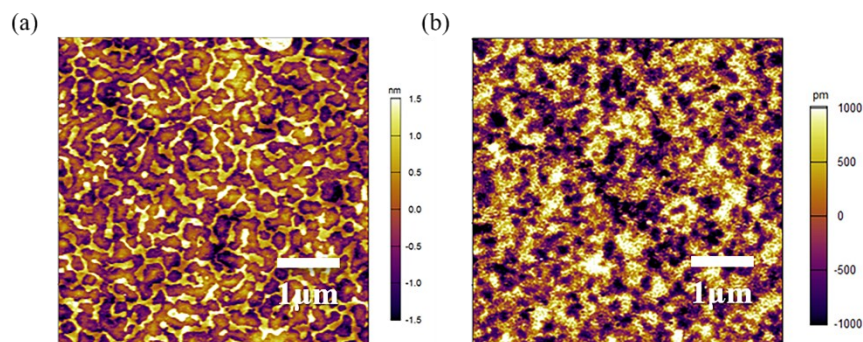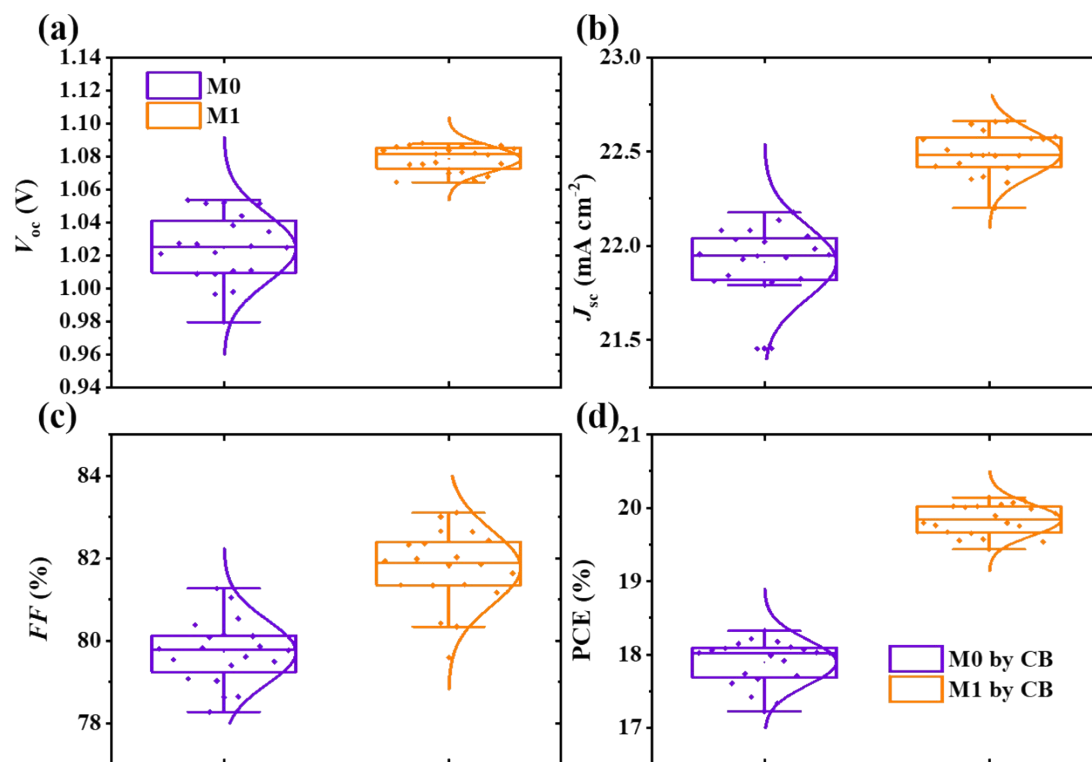
Fig. S10 XRD patterns of the perovskite films on M0 and M1

Table S3. The calculated crystal size from XRD data.

HTM/perovskite	Crystal size (110) (nm)
M0/perovskite	33.03
M1/perovskite	46.58

Fig. S11 Topographic AFM images of the HTM films for (a) M0 and (b) M1 spun from ethyl acetate solution

Fig. S12 (a)–(d) Statistics of photovoltaic parameters for the inverted PVSCs with M0 and M1 HTMs processed by CB. A total of 20 cells for each type of devices were used for statistics
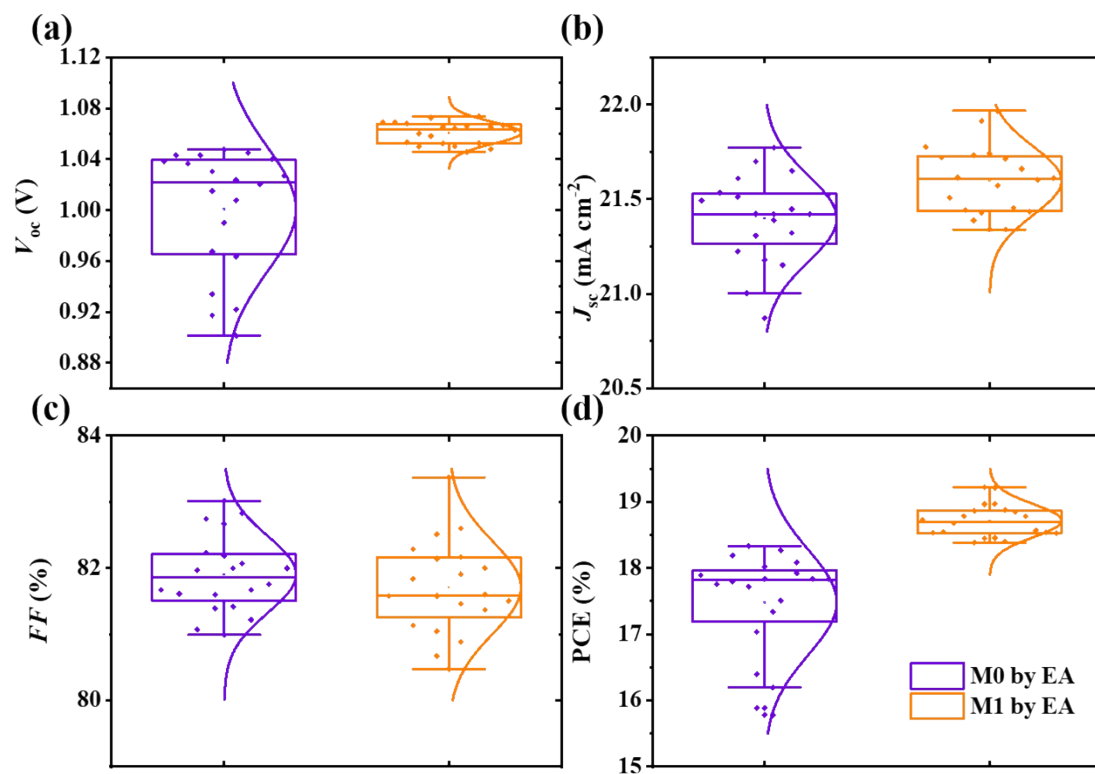
Fig. S13 (a)–(d) Statistics of photovoltaic parameters for the inverted PVSCs with M0 and M1 HTMs processed by EA. A total of 20 devices were used for statistics.