Noncovalent functionalization of hole-transporting materials with multi-walled carbon nanotubes for stable inverted perovskite solar cells

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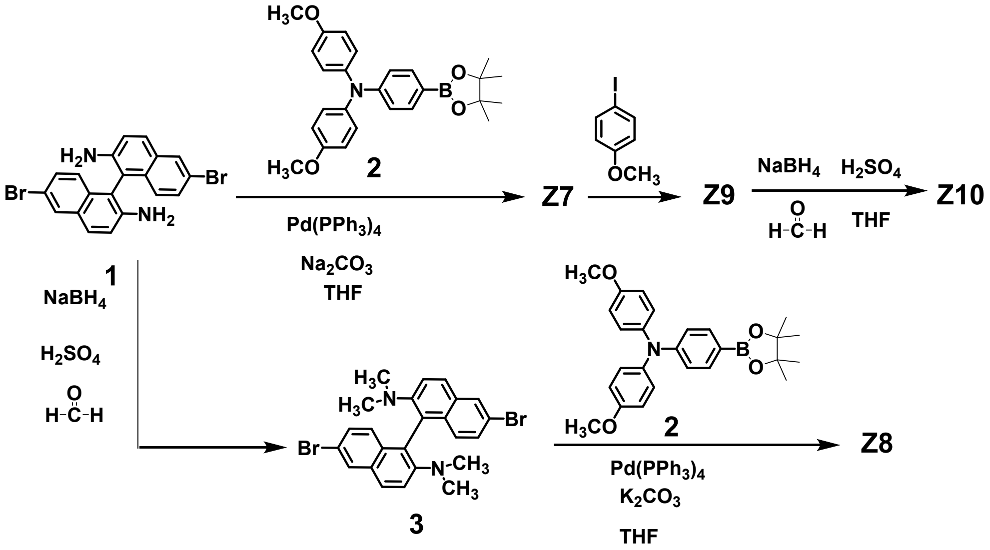
1 Synthesis routes of compounds **Z7-10**



Scheme S1 The synthesis routes of compounds **Z7, Z8, Z9 and Z10**.

The details of synthesis routes are shown as below:

Synthesis of 6,6'-dibromo-N^2,N^2,N$^{2'}$,N$^{2'}$-tetramethyl-[1,1'-binaphthalene]-2,2'-diamine (3) After adding 10 mL 20% H_2SO_4 and 1.3 mL 40% aq. formaldehyde to 5.0 mL tetrahydrofuran (THF) solution, 10 mL compound 1 solution (0.1 M in THF) and $NaBH_4$ (858.30 mg，23.00 mmol）were added simultaneously. The mixture was stirred for 30 min and then poured into 50 mL 2% aq. KOH solution and further extracted with ethyl acetate. The organic layer was dried by anhydrous $MgSO_4$ and evaporated. The crude product was purified by using column chromatography with petroleum ether/ethyl acetate (99:1, v/v) as eluent, and further recrystallized by petroleum ether to give a yellow powder with a yield of 51%.

Synthesis of 6,6'-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-N^2,N^2,N$^{2'}$,N$^{2'}$-tetramethyl-[1,1'-binaphthalene] -2,2'-diamine (Z8） Compound **3** (540 mg, 1.08 mmol), **2** (1216 mg，2.82 mmol), and Pd(P(Ph)$_3$)$_4$ (63 mg, 0.0545 mmol) were added in 15 mL THF solution under N_2 atmosphere, and the mixture was vigorously stirred for 5 min. Subsequently, a solution of Na_2CO_3 (400 mg，4.34 mmol) in 8 mL H_2O was added into the mixture. The resulting solution was stirred under reflux condition for 20 hours. The reaction mixture was washed with water and then extracted with ethyl acetate. The obtained organic layers were dried over with anhydrous sodium sulfate, and further purified by column chromatography with petroleum ether and ethyl acetate (5:1, v/v) as eluent. The obtained product was recrystallized from petroleum ether to give a yellow solid with a yield of 50%. ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ (ppm): 8.06 (s, 2 H), 7.98 (d, *J* = 8.8 Hz, 2 H), 7.53 ~ 7.50 (m, 6 H), 7.37 (d, *J* = 9.04 Hz, 2 H), 7.05 (d, *J* = 9.04 Hz, 8 H), 6.97 (d, *J* = 8.16 Hz, 2 H), 6.93 (d, *J* = 9.08 Hz, 8 H), 6.83 (d, *J* = 9.04 Hz, 4 H), 3.74 (s, 12 H), 2.44 (s, 12 H). ^{13}C NMR (400 MHz, *d*$_6$-DMSO) δ (ppm): 156.29, 149.76, 148.08, 140.47, 135.12, 133.34, 131.94, 130.15, 129.24, 127.62, 127.24, 126.48, 125.72, 125.18, 124.54, 121.40, 120.16, 115.52, 55.73, 43.64.

Synthesis of 6,6'-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-[1,1'-binaphthalene]-2,2'-diamine（Z7） Compound **1** (417 mg, 1.00 mmol), **2** (1059 mg，2.50 mmol), Pd(P(Ph)$_3$)$_4$ (54 mg, 0.05 mmol) were added in 15 mL tetrahydrofuran (THF) solution under N_2 atmosphere, and the mixture was vigorously stirred for 5 minutes. Subsequently, a solution of Na_2CO_3 (400 mg，4.00 mmol) in 8 mL H_2O was added into the mixture. The resulting solution was stirred under reflux condition for 20 hours. The reaction mixture was washed with water and then extracted with ethyl acetate. The organic layers were dried over anhydrous sodium sulfate. The crude product was purified by column chromatography with petroleum ether and ethyl acetate (2:1, v/v) as eluent. The obtained product was recrystallized with petroleum ether to give a light brown solid with a yield of 64 %. ^{1}H NMR (400 MHz, d_6-DMSO) δ (ppm): 7.97 (s, 2 H), 7.82 (d, J = 9.16 Hz, 2 H), 7.52 (d, J = 8.4 Hz, 4 H), 7.40 (d, J = 8.8 Hz, 2 H), 7.25 (d, J = 9.52 Hz, 2 H), 7.03 (d, J = 8.64 Hz, 8 H), 6.92 ~ 6.84 (m, 14 H), 4.73 (s, 4 H), 3.73 (s, 12 H). ^{13}C NMR (400 MHz, d_6-DMSO) δ (ppm): 156.10, 147.74, 144.55, 140.67, 133.12, 133.00, 128.11, 127.54, 126.97, 120.48, 119.40, 115.41, 110.82, 55.70.

Synthesis of 6,6'-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-N2,N2'-bis(4-methoxyphenyl)-[1,1'-binaphthalene] -2,2'-diamine （Z9） Compound **Z7** (300 mg，0.34 mmol), 4-Iodoanisole (237 mg, 1.01 mmol), $Pd_2(dba)_3$ (1.56 mg, 0.0017 mmol), 2-dicyclohexylphpsphino-2’,4’,6’-triisopropylbiphenyl (2.41 mg, 0.0015 mmol) and t-BuOk (115 mg, 1.03 mmol) were added in 10 mL t-BuOH solution under N_2 atmosphere, and the mixture was vigorously stirred at 95 ℃ for 30 hours. The reaction mixture was washed with water and then extracted with ethyl acetate. The organic layers were dried over anhydrous sodium sulfate. The crude product was purified by column chromatography with petroleum ether and ethyl acetate (1:1, v/v) as eluent. The product obtained was recrystallized from petroleum ether to give a yellow solid with a yield of 73%. ^{1}H NMR (400 MHz, d_6-DMSO) δ (ppm): 8.05 (s, 2 H), 7.91 (d, J = 10.80 Hz, 2 H), 7.54 (d, J = 7.20 Hz, 4 H), 7.45 (t, $J1$ = 8.64 Hz, $J2$ = 7.84 Hz, 4 H), 7.05 ~ 6.99 (m, 14 H), 6.92 (d, J = 7.20 Hz, 8 H), 6.84 (d, J = 8.08

Hz, 4 H), 6.79 (d, *J* = 8.52 Hz, 4 H), 6.48 (s, 2 H), 3.74 (s, 12 H), 3.68 (s, 6 H). ^{13}C NMR (400 MHz, *d*$_6$-DMSO) δ (ppm): 156.18, 155.21, 147.98, 142.30, 140.58, 136.53, 134.42, 133.34, 132.37, 129.61, 129.13, 127.62, 127.02, 125.72, 125.08, 123.13, 120.27, 118.65, 115.52, 114.76, 55.79.

Synthesis of 6,6'-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-N2,N2,N2',N2'-tetrakis(4-methoxyphenyl)-[1,1'- binaphthalene]-2,2'-diamine （**Z10**）After adding 3 mL 20% H_2SO_4 and 0.35 mL 40% formaldehyde to 5 mL THF, compound **Z9** (300 mg, 0.27 mmol) in THF (10 mL) and $NaBH_4$ (123.9 mg, 3.26 mmol）were added simultaneously. The mixture was stirred for 70 min and was then poured into 50 mL 2 % aq. KOH solution. The solution was extracted with ethyl acetate, and dried by $MgSO_4$ and evaporated. This crude product was purified by using column chromatography with 99:1 petroleum ether/ethyl acetate as eluent. The product obtained was recrystallized from petroleum ether to give a yellow solid with a yield of 13 %. ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ (ppm): 8.02 (s, 2 H), 7.74 (d, *J* = 8.00 Hz, 2 H), 7.09 (d, *J* = 8.00 Hz, 2 H), 7.00 (d, *J* = 4.00 Hz, 4 H), 6.91 (d, *J* = 8.00 Hz, 9 H), 6.77 (d, *J* = 8.00 Hz, 9 H), 6.67 ~ 6.61 (m, 6 H), 6.35 (d, *J* = 8.00 Hz, 4 H), 6.28 (d, *J* = 8.00 Hz, 4 H), 3.62 (s, 18 H), 2.41 (s, 6 H). ^{13}C NMR (400 MHz, *d*$_6$-DMSO) δ (ppm): 156.26, 152.44, 148.20, 146.62, 143.04, 140.28, 136.05, 132.95, 131.92, 130.75, 129.89, 129.73, 127.25, 124.28, 119.75, 116.98, 115.34, 113.95, 55.65, 55.51.

2 Fabrications of i-PSCs

2.1 Materials

Indium-doped tin dioxide doped glass (ITO) substrates were purchased from Hartford Glass Company. PbI_2 and $PC_{61}BM$ were purchased from p-OLED (China), MAI was purchased from Dye-sol company, and the dimethyl formamidine, dimethyl sulfoxide and chlorobenzene were purchased from Sigma Aldrich. All reagents and solvents were used without further purification.

Preparation of HTMs attached onto MWCNTs (HTM@MWCNTs). 0.01 mg MWCNTs were dispersed in N-Methyl pyrrolidone (1 mL) containing 5 mg HTM in a sonicator for 3 h and stirred for 1 h.

Preparation of perovskite precursor solution. PbI_2 (461 mg), MAI (159 mg), and DMSO (78 mg) were added in 600 mg DMF. The solution was heated and stirred at 60 ^{o}C for 60 min.

2.2 Device Fabrication

ITO substrates were cleaned by ultrasonic bathe in detergent, deionized water, acetone and ethanol for 15 min sequentially, further cleaned under ozone (UV-Ozone) for 30 min. The HTMs solution with the concentration of 5 mg/mL in CB were spin-coated on the ready ITO substrates. The substrates coated with HTM precursor liquid film were annealed at 100 ^{o}C for 15 min. After cooled for 10 minutes, the substrates were transferred into the vacuum glove box. The preparation perovskite precursor solution was filtered and spin-coated on the surface of HTMs layer at 4000 rpm for 25 s, and CB was poured on the spinning substrate at 15 s. The substrates were heated at

100 °C for 10 min to obtain a dense film. Afterwards, $PC_{61}BM$ solution in CB with a concentration of 20 mg/mL was deposited at 4000 rpm for 30 s, and annealed at 100 °C for 10 min. Subsequently, BCP (0.5 mg/mL in IPA) was spin-coating as a buffer layer. Eventually, 80 nm Ag as mental electrode were evaporated onto the top of BCP layer.

3 Characterizations of HTMs and i-PSCs

3.1 Density functional theory (DFT) calculation

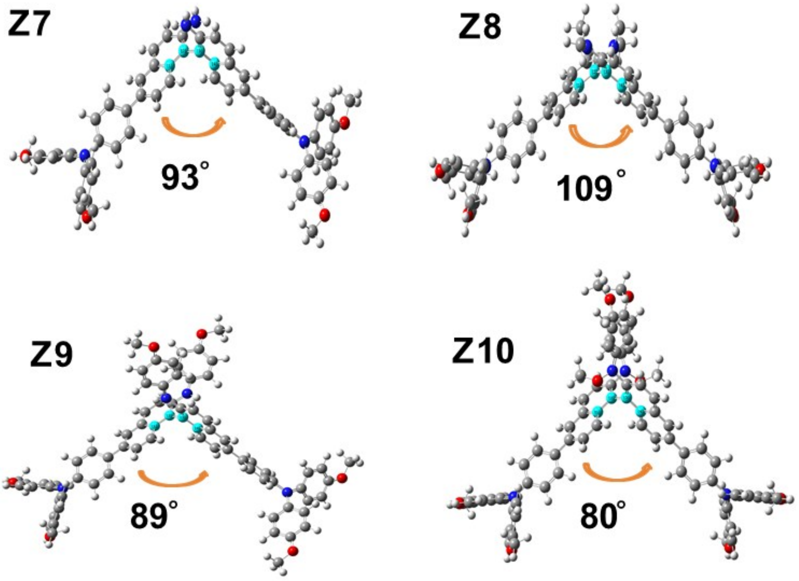


Fig. S1 The obtained dihedral angles of Z7-10 by using DFT calculation.

3.2 Differential scanning calorimetry (DSC)

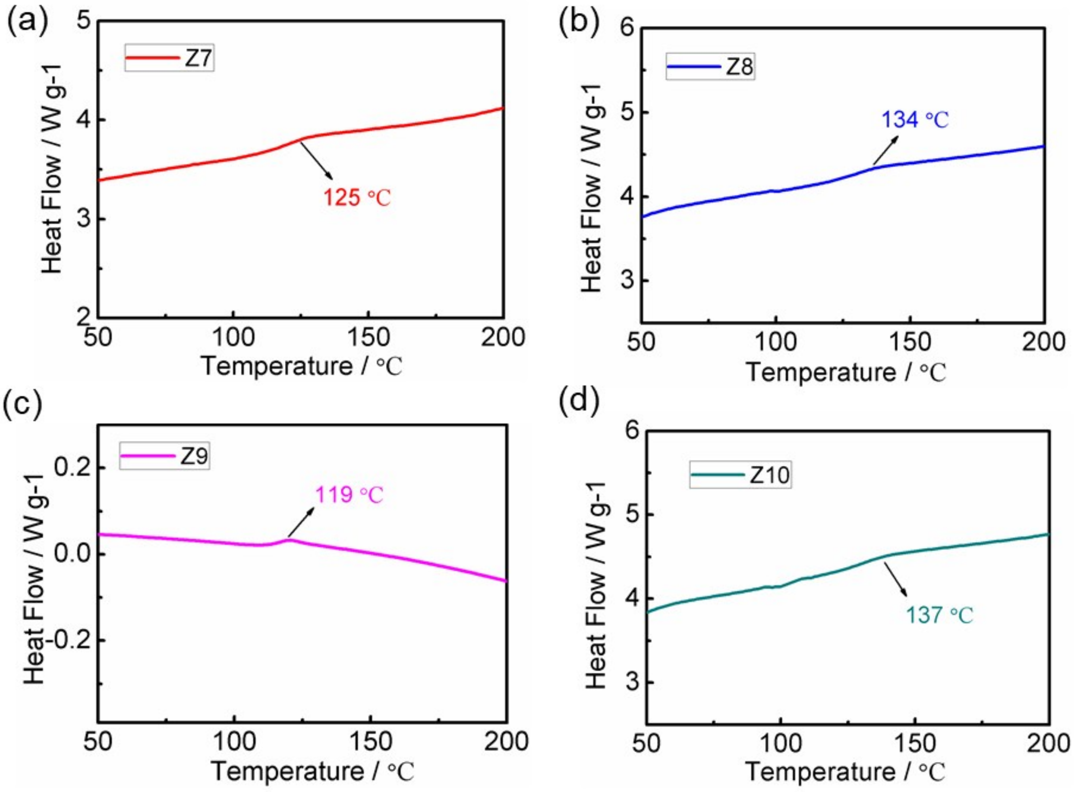


Fig. S2 Differential scanning calorimetry (DSC).

DSC measurement was conducted on NETZSCH DSC 200 F3 differential scanning calorimeter heating from 20 °C to 200 °C.

3.3 Cyclic voltammetry measurements

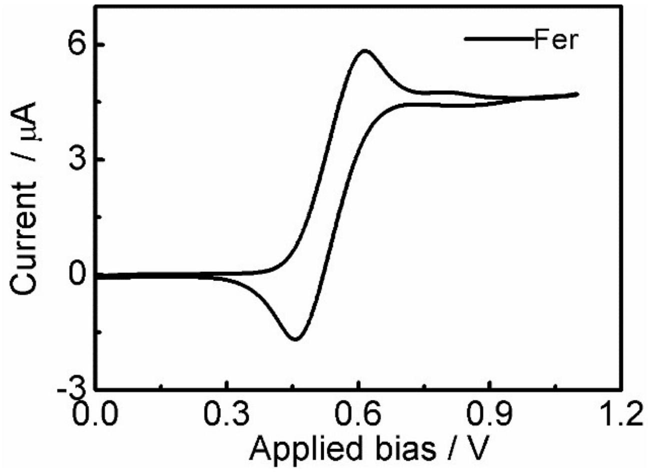


Fig. S3 Cyclic voltammograms of ferrocene.

Table S1 Detailed optoelectronic properties of the HTMs Z7, Z8, Z9 and Z10.

HTM	λ_{int} *(nm)*	λ_{max} *(nm)*	E_{0-0} (eV)	E_{ox} vs (Ag/AgCl) (V)	E_{HOMO} vs (Ag/AgCl) (eV)	E_{LUMO} vs (Ag/AgCl) (eV)
Z7	399	341	3.11	0.80	-5.29	-2.18
Z8	407	342	3.05	0.86	-5.35	-2.30
Z9	413	350	3.00	0.80	-5.29	-2.29
Z10	425	348	2.92	0.82	-5.31	-2.39

The absorption spectra of the solution of HTMs (dissolve in DCM) were recorded on a SHIMADZU UV-2600 spectrophotometer. Fluorescence-emission measurements were obtained on a HITACHI F–4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) was measured on a CHI660D electrochemical workstation with a three-electrode electrochemical cell composed of a platinum electrode (counter electrode), Ag/AgCl electrode (reference electrode) and a glassy carbon disk (working electrode) at a scan rate of 10 mV s^{-1} in DCM solution containing 0.1 M of n-Bu_4NPF_6 and all potentials were reported against the ferrocene/ferrocenium (Fc/Fc^+) reference.

3.4 Scanning electron microscope (SEM) measurements

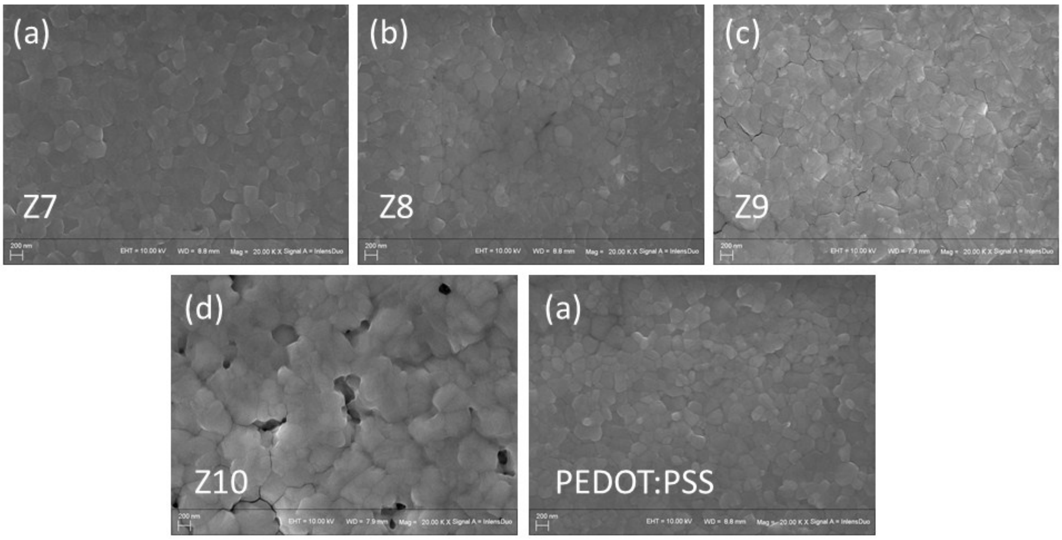


Fig. S4 SEM images of perovskite coated on the surface of corresponding HTMs.

3.5 *J-V* measurements

Table S2 Two batches of parallel stability tests based on Z7 and Z8@MWCNT.

The first batch						
Date	Z7			Z7@MWCNT		
	PCE /%	*FF*	*Jsc /mA cm-2*	*PCE /%*	*FF*	*Jsc /mA cm-2*
Mar. 16, 2019	16.50	0.73	22.32	16.16	0.72	22.41
Mar. 20, 2019	14.99	0.65	21.59	9.52	0.63	14.59
Mar. 22, 2019	12.93	0.63	20.35	8.25	0.56	15.88
Mar. 24, 2019	12.37	0.66	18.26	8.66	0.55	17.86
Mar. 26, 2019	11.33	0.64	16.41	4.41	0.40	15.62
Mar. 30, 2019	10.16	0.61	15.56	4.02	0.38	15.25
The second batch						
Date	Z7			Z7@MWCNT		
	PCE /%	*FF*	*Jsc /mA cm-2*	*PCE /%*	*FF*	*Jsc /mA cm-2*
Mar. 16, 2019	15.84	0.69	22.53	16.17	0.72	22.67
Mar. 20, 2019	15.09	0.65	22.38	10.07	0.64	15.43
Mar. 22, 2019	12.66	0.63	19.64	8.90	0.60	15.69
Mar. 24, 2019	12.89	0.63	19.77	8.51	0.58	15.74
Mar. 26, 2019	11.66	0.62	18.30	6.29	0.50	16.84

Mar. 30, 2019	11.25	0.61	18.23	5.14	0.45	14.69

Reverse scan, from 1.2 V to 0 V.

Table S3 Two batches of parallel stability tests based on Z8 and Z8@MWCNT.

The first batch						
	Z8			Z8@MWCNT		
Date	*PCE /%*	*FF*	*Jsc /mA cm-2*	*PCE /%*	*FF*	*Jsc /mA cm-2*
Mar. 16, 2019	14.86	0.67	21.78	14.48	0.64	21.59
Mar. 20, 2019	13.11	0.65	20.22	6.71	0.37	20.69
Mar. 22, 2019	12.83	0.67	20.94	8.26	0.45	17.95
Mar. 24, 2019	12.69	0.67	21.63	4.95	0.36	18.59
Mar. 26, 2019	11.51	0.66	20.07	2.94	0.37	17.06
Mar. 30, 2019	11.33	0.65	20.31	3.78	0.44	18.23
The second batch						
	Z8			Z8@MWCNT		
Date	*PCE /%*	*FF*	*Jsc /mA cm-2*	*PCE /%*	*FF*	*Jsc /mA cm-2*
Mar. 16, 2019	14.76	0.68	21.45	13.28	0.60	21.43
Mar. 20, 2019	12.34	0.53	12.34	8.47	0.45	21.35
Mar. 22, 2019	12.88	0.59	12.88	2.76	0.33	19.66
Mar. 24, 2019	12.68	0.60	12.68	8.87	0.46	20.26
Mar. 26, 2019	11.67	0.60	11.67	8.97	0.45	18.96
Mar. 30, 2019	10.43	0.54	10.43	2.18	0.36	20.10

Reverse scan, from 1.2 V to 0 V.

The current density-voltage *(J-V)* characterization was measured using a standard xenon lamp based solar simulator (Oriel Sol 3A, USA) under simulated AM 1.5 irradiation (100 mW• cm^{-2}) and a digital source meter (Keithley 2400). The *J-V* measurement was performed at a forward scan rate of 0.1 V/s. Light intensity of solar simulator was verified by using Oriel P/N 91150 V, KG-5 visible light filter calibrated by national renewable energy laboratory (NREL). All experiments were carried out in air.

The device stability was tested without encapsulation in a dark condition.

3.6 Scanning electron microscope (SEM) measurements

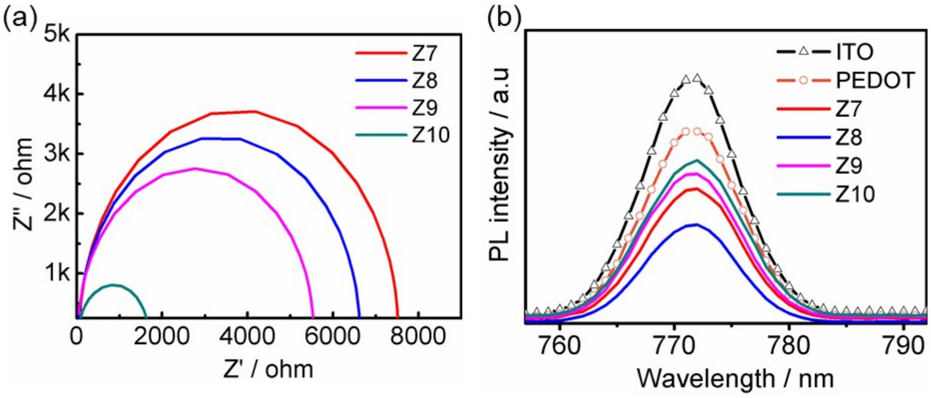


Fig. S5 (a) Electrochemical impedance spectroscopy (EIS); (b) Steady state photoluminescence (PL) spectrum of perovskite films on different substrates (ITO only, ITO/corresponding HTM).

Steady-state photoluminescence (PL) tests were conducted on a HITACHI F–4500 fluorescence spectrophotometer with a excitation peak at 500 nm**.**

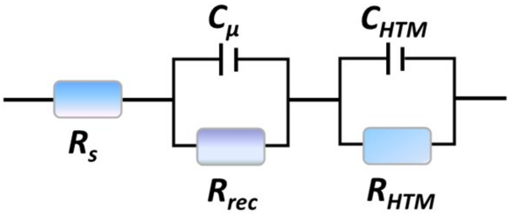


Fig.S6 Equivalent circuit used to fit the impedance spectra. R_s is the series resistance accounting for the transport resistance of the TCO and the PCBM layer. C_{HTM} and R_{HTM} are the HTM capacitance and the HTM resistance. C_μ and R_{rec} are the chemical capacitance and the charge recombination resistance at the SnO_2/HTM interface.

3.7 IR spectra measurement

2 mg MWCNTs were dispersed in N-Methyl pyrrolidone (80 mL) containing 0.125

mg HTM in a sonicator for 3 h and stirred for 1 h. MWCNTs suspension dissolving with HTMs was vacuum-filtered through 0.45 μm nylon membrane filter. The filter residue was dried at 80 ℃ for 24 h in vacuum oven to give the samples for FT-IR measurement. 0.5 mg samples was fully grinded in the mold, and 50 mg dried KBr powder was added. This mixture continued to grind until the sample was mixed evenly. Subsequently，the mixture was pressed at a pressure of (5~10)×10^7 Pa to form a transparent thin film for determination.

3.8 UV-vis absorption spectrum of pristine MWCNT, Z7 and Z8 attached to MWCNTs, and pristine Z7 and Z8 in N-methyl-pyrrolidone

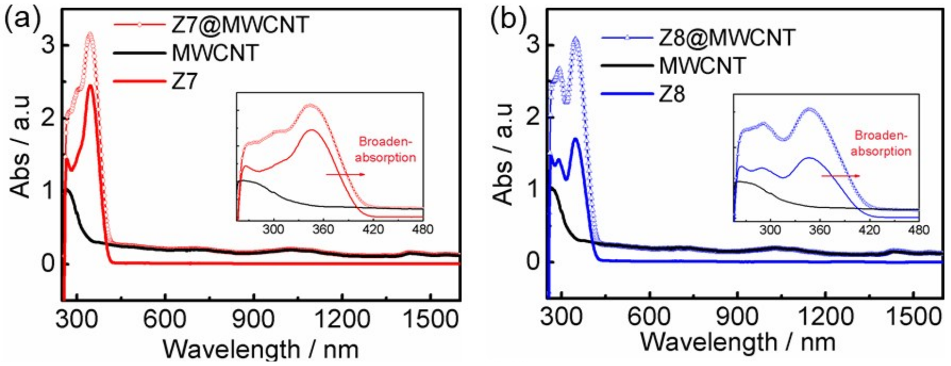


Fig. S7 The UV-vis absorption spectrum of pristine MWCNT, Z7 and Z8 attached to MWCNTs, and pristine Z7 and Z8 in N-methyl-pyrrolidone.

3.9 AFM measurement

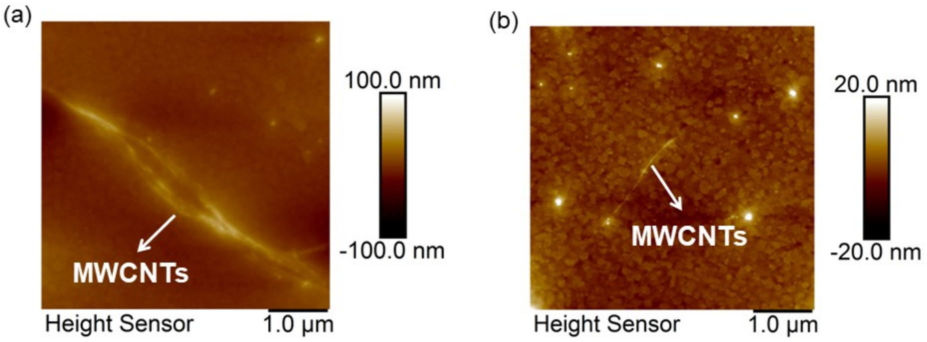


Fig. S8 2D surface AFM images of Z7 films with (a) a cluster of MWCNTs and (b)

2~3 MWCNTs. The AFM images illustrated good organo-dispersible MWCNT. And a noncovalent functionalization is existed between HTMs and MWCNT.

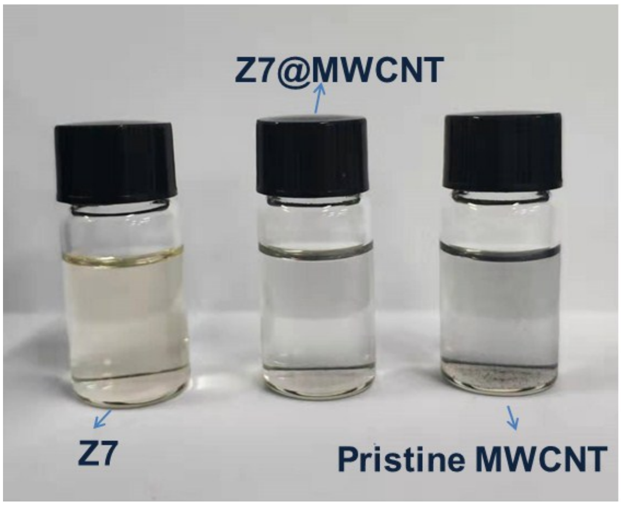
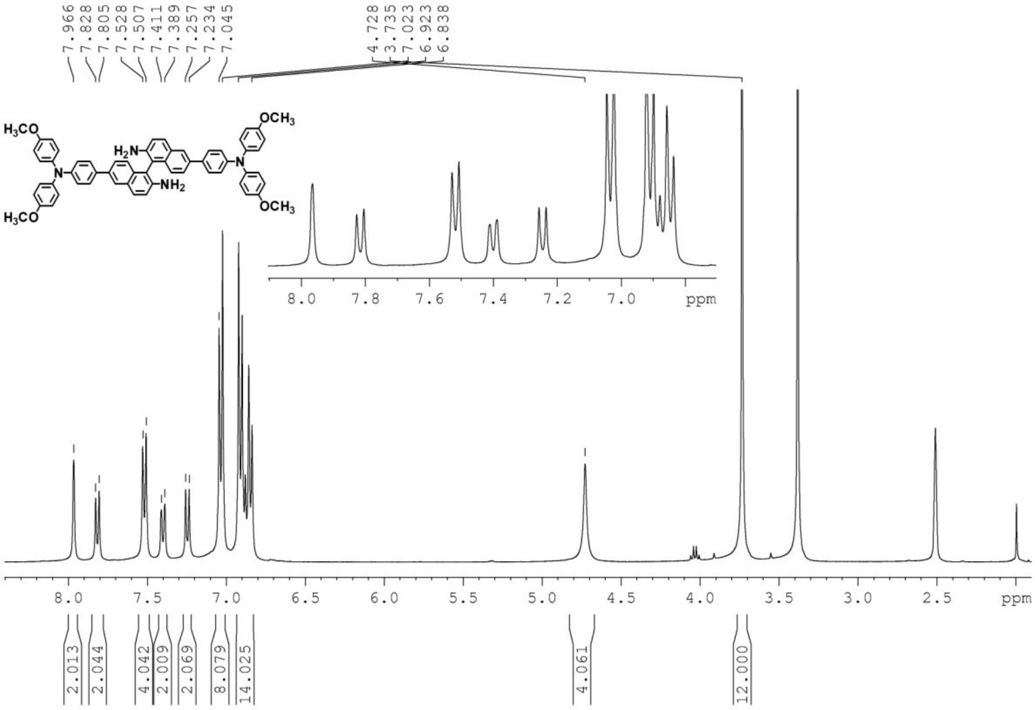
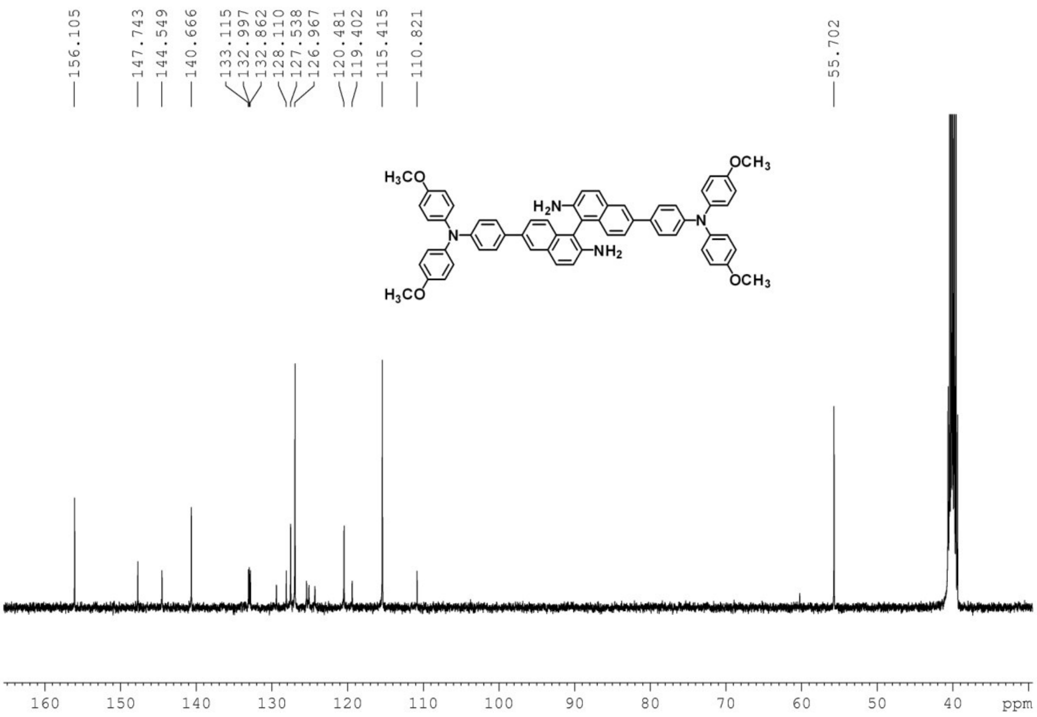


Fig. S9 Photos of the solution with Z7, Z7@MWCNT, and pristine MWCNTs in N-methyl-pyrrolidone stored for three days after physisorption treatment.

4 ^{1}H NMRand ^{13}C NMR spectra of Z7, Z8, Z9 and Z10

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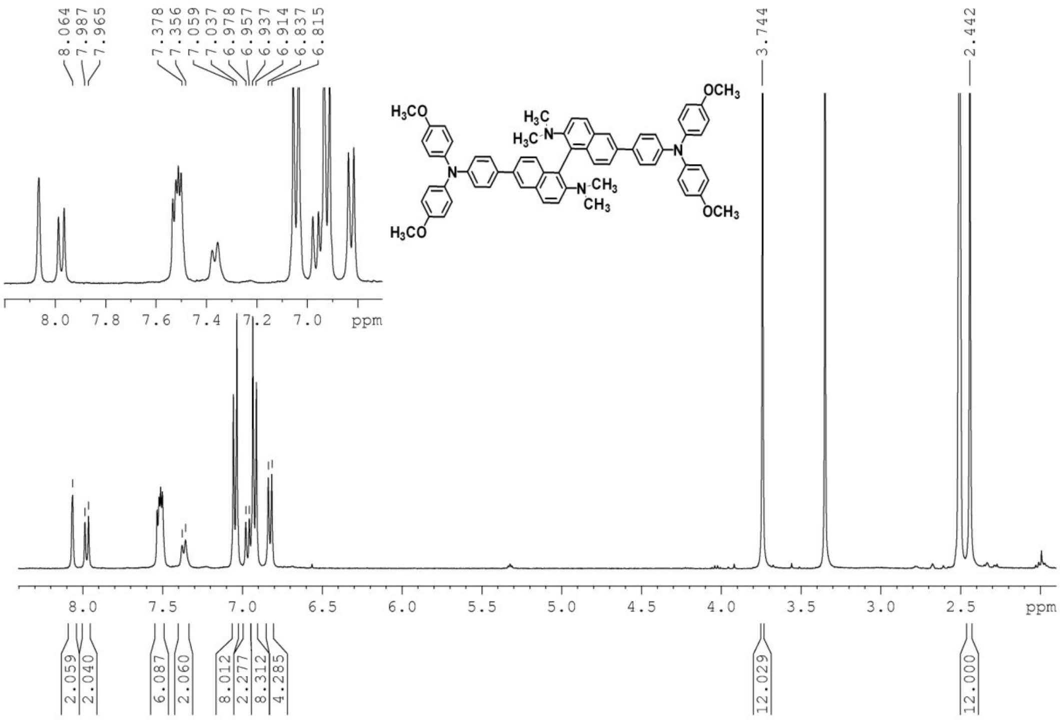
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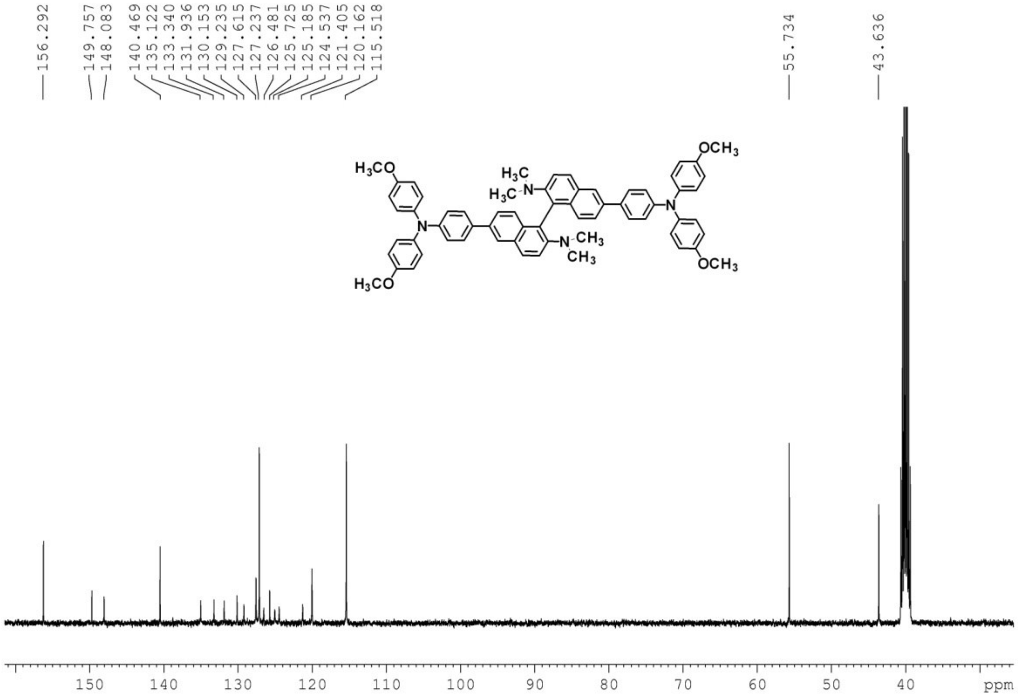
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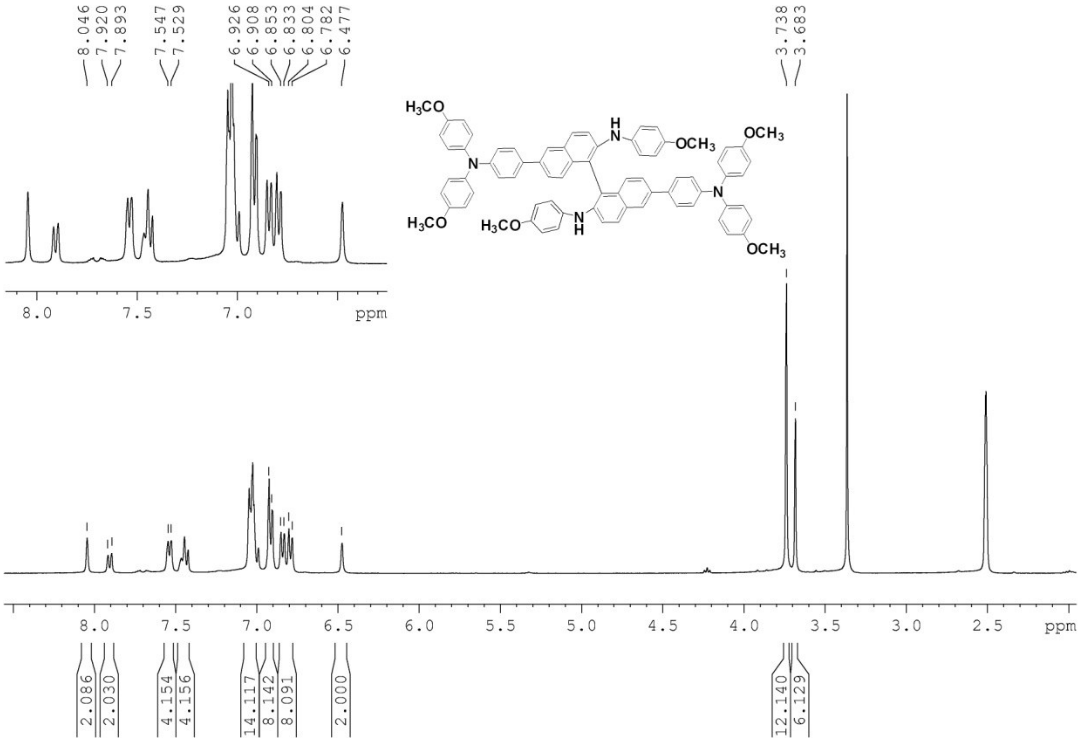
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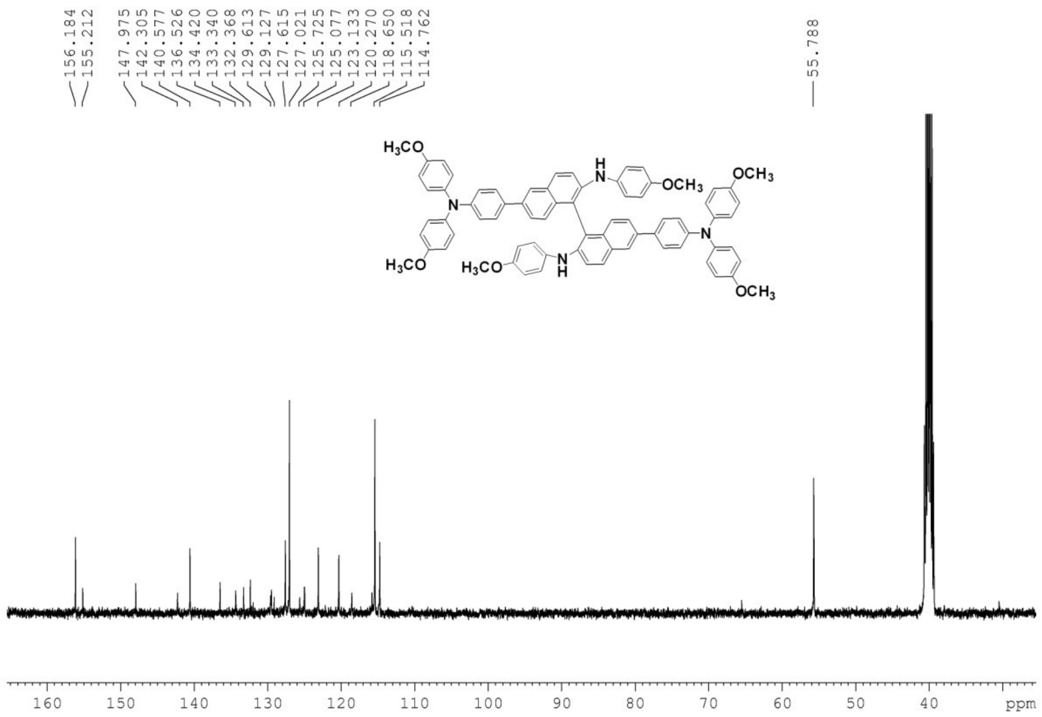
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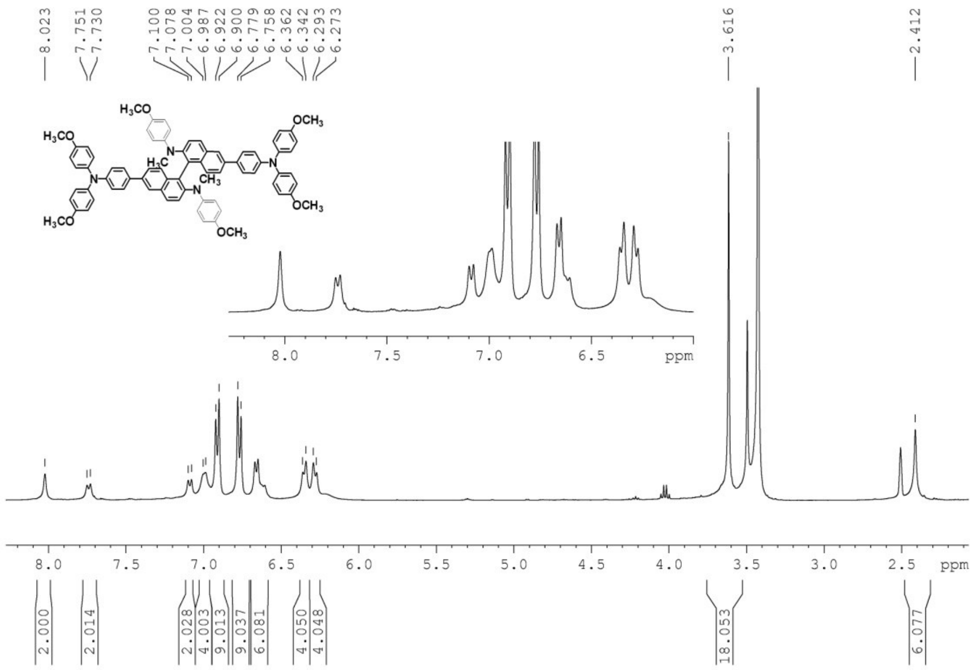
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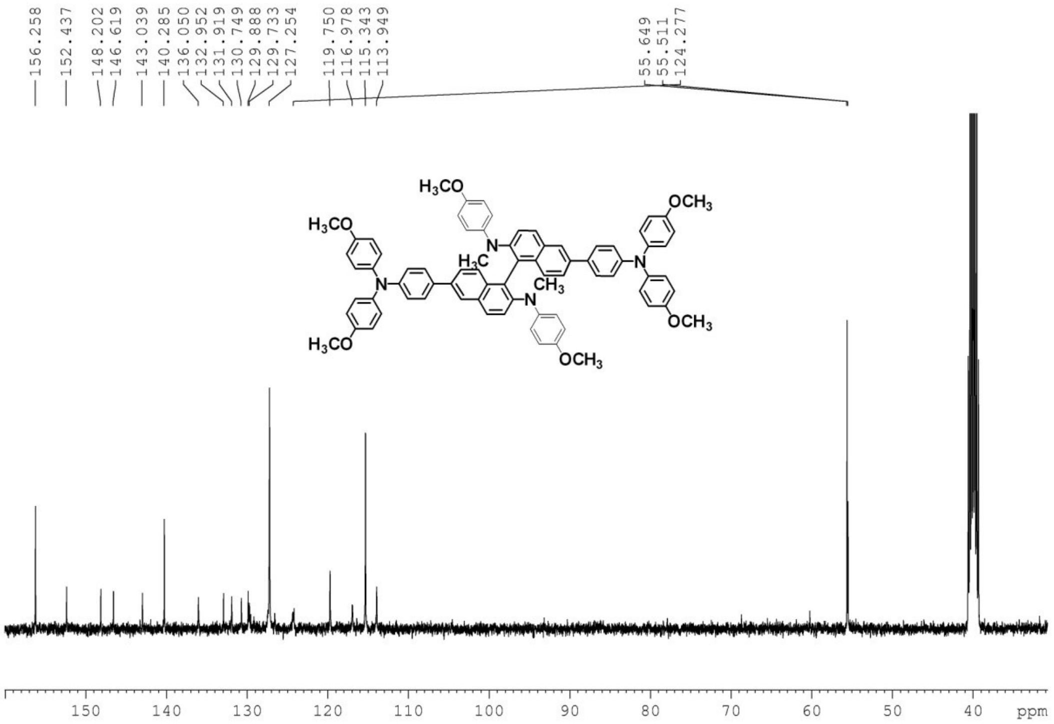
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