Lewis-Base Containing spiro Type Hole Transporting Materials for High-Performance Perovskite Solar Cells with Efficiency Approaching 20%

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1. Experimental section

1.1, Device fabrication and characterization

Materials: SnO₂ colloid precursor (tin (IV) oxide, 15% in H₂O colloidal dispersion) was purchased from Alfa Aesar. Lead iodide (99.99%) was purchased from TCI, lead bromide (99.999%) and cesium iodide (99.9%) were bought from Sigma-Aldrich. Formamidinium iodide (FAI) and methylammonium bromide (MABr) were synthesized by reacting formamidine acetate (Aladdin) and hydroiodic acid (55.0-58.0 wt% in H₂O, Aladdin), methylamine (30-33 wt% in ethanol, Aladdin) and hydrobromic acid (48 wt% in H₂O, Aladdin), respectively. The particular experimental operations were referred to as previously reported methods.¹ spiro-OMeTAD was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.

Fabrication of the devices: The glass substrates (Nippon Sheet Glass) including FTO layer were chemically etched, cleaned with deionized water, acetone, and anhydrous ethanol for 15 min, respectively. Then, after the dry clean substrates were treated by plasma for 10 min, a thin layer of SnO₂ nanoparticle film (SnO₂ colloid precursor diluted by deionized water, 1: 3, weight ratio) were spin-coated on the FTO substrates at 3000 rpm for 30 s and annealed in ambient air at 150 °C for 30 min. Next, a CsFAMA triple-cation "mixed" perovskite precursor solution was prepared by dissolving PbI₂ (1.15 M), FAI (1.05 M), PbBr₂ (0.195 M) and MABr (0.2 M) in a mixed solvent of anhydrous DMF and DMSO (4:1, volume ratio). After stirring for 30 min, 57.5 μL CsI which was previously dissolved as a 1.5 M stock solution in DMSO was added to the mixed perovskite precursor solution. Then, the perovskite precursor solution was spin-coated onto the substrates with SnO₂ via using a two steps procedure (the first step is under 1000 rpm for 10 s and the second step is under 5000 rpm for 30

s) in a nitrogen glove box. When entering the last 5 seconds before the second step finish, the antisolvent (150 μ L of chlorobenzene) were dropped on the spinning substrate.² The substrates were then annealed on a hotplate at 100 °C for 60 min. Afterwards, the substrates were cooled to room temperature, and the solution with different HTMs were spin-coated on different substrates containing perovskite layers at 4000 rpm for 30 s. For spiro-OMeTAD solution, 72.3 mg of spiro-OMeTAD was dissolved 1 mL of chlorobenzene with additives of 17.5 μ L of bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich) solution (520 mg mL⁻¹ in acetonitrile), 28.5 μ L of 4-tertbutylpyridine (TBP, Sigma-Aldrich). For spiro-CN and spiro-PS solution, 60 mg of each HTM was dissolved 1 mL of chlorobenzene with additives of 14 μ L of Li-TFSI solution (520 mg mL⁻¹ in acetonitrile), 23 μ L of TBP. Finally, 70 nm of the gold counter electrode was thermally evaporated under high vacuum.

Device Characterization: The surface morphology was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The top-view and cross-sectional view morphology of the perovskite films were observed using a field-emission scanning electron microscope (SEM, Apreo S). The roughness of the films was recorded using atomic force microscopy (AFM, Multimode-8J, America). Photoluminescence was measured at room temperature on a fluorescence spectrophotometer (FLS980, Edinburgh Instruments). The steady-state PL emissions were measured under 460 nm light source excitation using monochromatized Xe lamp, while the time-resolved PL decays were carried out with a pulsed diode laser excitation source. The photovoltaic performance of devices was measured with a Keithley 2401 source meter using a solar simulator (SS-F5-3A, Enlitech) at 100 mW cm⁻² illumination (AM 1.5 G) equipped with a calibrated Si reference cell (SRC-2020, Enlitech). The J–V curves of the PSCs were measured in reverse scan (from 1.2 to -

0.1 V) or forward scan (from -0.1 to 1.2 V) modes at a scan speed of 200 mV s⁻¹. The active area of devices was defined by a metal shadow mask of 0.1 cm². External quantum efficiency (EQE) was obtained on a computer-controlled quantum efficiency measuring instrument (QE-R, Enlitech). Electrochemical impedance spectroscopy (EIS) measurements were carried out under 10 mW cm⁻² illumination at applied voltages (0.7 V) using an electrochemical workstation (Zennium Zahner, Germany) with an AC perturbation of 10 mV ranging from 100 mHz to 1 MHz, at room temperature with 40% humidity. Stability test: The dark long-term stability assessment of the perovskite solar cells was carried out by repeating the *J-V* characterizations over various times. The unsealed devices were stored under ambient atmosphere with 10-30% relative humidity at room temperature. Space-charge-limited current (SCLC) measurement based on the hole-only devices (ITO/PEDOT:PSS/HTM/Au); the dark J-V characteristics of the devices were measured by a Keithley 2401 source meter in the range of 0-5 V. The hole mobility (μ) can be extracted from the trap-free SCLC regime, according to Mott-Gurney law:

$$J_D = \frac{9\mu\varepsilon_r\varepsilon_0 V_b^2}{8L^3} \tag{S1}$$

Where J_D is the current density, V_b is applied voltage, L is the thickness of HTM film, ε_r is the relative dielectric constant of organic materials (ε_r =3), ε_0 is the vacuum permittivity, and q is the electron charge.³

1.2、DFT calculation

Density functional theory (DFT) geometry optimization of all compounds were performed using the B3LYP functional and 6-31g(d) basis set in the Gaussian 09 program package. Stationary points were verified by frequency analysis. The optimized structures were found to be stable. Solvent contributions

to energies were included with the SMD solvent model in DCM by performing single point calculations at the previously optimized geometry.

1.3、Synthetic details

1.3.1 Synthetic route



Fig S1. Synthetic route to spiro-PS and spiro-CN. Reagents and conditions: i) $Pd(dba)_2$, tri-tbutylphosphine, potassium t-butoxide, toluene, reflux for 12h; ii) $P(OEt)_3$, reflux overnight; iii) TiCl₄, pyridine, chlorobenzene, 80 °C overnight; iv) Lawesson's reagent, toluene, relux for 5h.

1.3.2 Synthetic procedure

4,4'-dimethoxydiphenylamine (1). In a 250 ml round bottom flask, 4-methoxyphenylamine (0.92 g, 7.5 mmol), 1-iodo-4-methoxybenzene (1.17 g, 5.0 mmol), CuI (0.095 g, 0.5 mmol), K₂CO₃ (1.38 g, 10.0 mmol), and L-proline (0.12 g, 1.0 mmol) were dissolved with 3 mL of DMSO .Then the mixture was stirred at 90 °C for 24 h. After cooled, the mixture was extracted with water and ethyl acetate. The organic layer was separated, washed with saturated NaCl solution, dried over MgSO₄, and evaporated in vacuo. The crude product was purified by column chromatography eluting with a 1:4 mixture of ethyl acetate and hexane and recrystallized with n-hexane to obtain a white crystal (0.90 g, 78.9%). ¹H-NMR (500 MHz, CDCl₃): 6.89 (d, J = 8.1 Hz, 4H), 6.79 (d, J = 8.7 Hz, 4H), 3.67 (s, 6H).

2,7-bis(bis(4-methoxyphenyl)amino)-fluoren-9-one (2). A mixture of 4,4'-dimethoxydiphenylamine (5.0 g, 21.8 mmol), Pd(dba)₂ (629 mg, 1.1 mmol), tri-t-butylphosphine (442 mg, 2.2 mmol), potassium t-butoxide (65.4 g, 7.3 mmol), 2,7-dibromofluorenone (3.5 g, 10.4 mmol) and toluene (100 mL) was refluxed in a 250 ml flask for 12 h. After cooled to RT and then concentrated., the residue was dissolved in CH₂Cl₂, and extracted with CH₂Cl₂ and water. The organic layer was dried over MgSO₄ and concentrated. Purification by column chromatography with a 1:4 mixture of ethyl acetate and hexane gave a dark-blue solid (5.6 g, 84%).¹H-NMR (500 MHz, CDCl₃): δ 7.17 (d, J = 2.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 9.0 Hz, 8H), 6.94 (dd, J = 8.2, 2.3 Hz, 2H), 6.83 (d, J = 9.0 Hz, 8H), 3.80 (s, 12H).

2,2',7,7'-tetrakis(bis(4-methoxyphenyl)amino)-10'H-spiro[fluorene-9,9'-phenanthren]-10-one (3). 2,7-bis(bis(4-methoxyphenyl)amino)-fluoren-9-one (2.0 g, 3.15 mmol) and P(OEt)₃ (10 mL, 58 mmol) were mixed in a flask (250 mL), then the reaction mixture was heated to reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (eluent: ethyl acetate/petroleum ether/dichloromethane 1:1:4) to afford the target material (51%, 1.0 g). ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 2.3 Hz, 2H), 7.04 (d, J = 8.9 Hz, 9H), 6.90 (d, J = 8.5 Hz, 8H), 6.83 (d, J = 8.9 Hz, 8H), 6.76 (d, J = 8.7 Hz, 8H), 6.70 (d, J = 8.1 Hz, 3H), 6.49 (s, 2H), 3.79 (s, 14H), 3.72 (s, 10H). MS (MALDI-TOF) m/z: 1252.2.

2,2',7,7'-tetrakis(bis(4-methoxyphenyl)amino)-10'H-spiro[fluorene-9,9'-phenanthren]-10-alkenylmalononitrile (spiro-CN-OMeTAD) (4). A dry flask under nitrogen was charged with compound 3 (0.18 g, 0.143 mmol), malononitrile (0.715 mmol), and dry chlorobenzene (10 mL). TiCl₄ (1.287 mmol) was added dropwise, followed by pyridine (1.859 mmol). The mixture was heated at 80°C overnight. Then CH₂Cl₂ was added to the mixture, and the organic layer was washed three times with H₂O. The organic layer was dried with MgSO₄, filtered, and evaporated. Purification by silica gel column chromatography (DCM/EA/hexanes 1:1:6 v/v) followed by precipitation in MeOH afforded compound as an indigo blue solid (24 %, 44.6 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H), 7.24 (s, 2H), 7.04 (d, J = 8.8 Hz, 9H), 6.94 (dd, J = 8.8, 2.3 Hz, 2H), 6.86 (dd, J = 6.7, 2.2 Hz, 14H), 6.75 (d, J = 8.9 Hz, 8H), 6.70 (s, 3H), 6.29 (s, 2H), 3.80 (s, 14H), 3.73 (s, 10H). ¹³C NMR (850 MHz, CDCl₃) δ 175.85, 156.68, 156.05, 155.79, 148.19, 147.24, 146.83, 140.18, 139.55, 128.59, 127.53, 127.48, 126.36, 125.21, 124.12, 124.04, 123.57, 120.11, 119.59, 118.35, 118.05, 115.13, 114.72, 79.85, 62.56, 55.60, 55.54. MS (MALDI-TOF) m/z: 1306. Anal. Calcd for C₈₅H₆₈N₆O₈: C, 78.44; H,5.27; N, 6.46. Found : C, 78.87; H, 5.16; N, 6.49.

2,2',7,7'-tetrakis(bis(4-methoxyphenyl)amino)-10'H-spiro[fluorene-9,9'-phenanthren]-10'-thione

(*spiro-PS-OMeTAD*) (5). Compound 3 (0.1 g, 1.0 equiv) was treated with Lawesson's reagent (1.5 equiv) in dry toluene (10 ml), and the orange solution was refluxed until starting material was consumed (TLC monitoring). Then the solvent was removed under vacuo and the dark blue residue was partitioned between H₂O and ethyl acetate. The dark blue phase was washed with H₂O (2*20 ml), brine (3*20 ml), dried over Na₂SO₄, filtered-off, concentrated under vacuo and purified by silica gel column chromatography eluting with ethyl acetate/CH₂Cl₂/hexane solution(1:1:6) to afford the product as a dark blue solid (19.7%, 20 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 2.5 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.9 Hz, 9H), 6.99 (d, J = 2.6 Hz, 1H), 6.91 (d, J = 8.8 Hz, 8H), 6.82 (d, J = 8.9 Hz, 8H), 6.75 (d, J = 8.8 Hz, 8H), 6.69 (d, J = 7.7 Hz, 2H), 6.55 (s, 2H), 3.79 (s, 14H), 3.71 (s, 10H). ¹³C NMR (850 MHz, CDCl₃) δ 189.60, 156.13, 155.89, 147.14, 140.48, 140.36, 139.53, 126.72, 126.46, 126.27, 124.63, 124.55, 123.12, 119.97, 119.83, 118.42, 118.04. 114.91, 114.67, 55.63, 55.69, 55.52, 55.49. MS (MALDI-TOF) m/z: 1268.3. Anal. Calcd for C₈₂H₆₈N₄O₈S : C, 77.58; H,5.40; N, 4.41; S, 2.53. Found : C, 77.79; H, 5.42; N, 4.52; S, 2.51.

2、Results and Discussion

2.1 ¹H-NMR, ¹³C-NMR and MALDI-TOF MS spectra

2.1.1 ¹H-NMR







Fig S3. ¹H NMR spectrum of compound 3



Fig S4. ¹H NMR spectrum of spiro-CN





2.1.2 ¹³C-NMR



Fig S6. ¹³C NMR spectrum of spiro-CN







Fig S8. MADLI-TOF mass spectrometry for compound 3



Fig S9. MADLI-TOF mass spectrometry for spiro-CN



Fig S10. MADLI-TOF mass spectrometry for spiro-PS

2.2 Fourier transform infrared (FTIR) spectroscopy



Figure S11 FTIR spectra of spiro-CN, spiro-PS and spiro-PT.

2.3 Packings structures and crystallographic parameters

2.3.1 Packings structures



Figure S12 Noncovalent intermolecular short contacts of spiro-CN were marked with blue dash lines.

2.3.2 Crystallographic parameters

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	spiro-CN	spiro-PS	spiro-OMeTAD
Empirical formula	C ₈₅ H ₆₈ N ₆ O ₈	$C_{82}H_{68}N_4O_8S$	$C_{81}H_{68}N_4O_8$
Formula weight	1393.58	1269.45	1225.455
Crystal color, habit	Indigo Blue, needle	Dark Blue, needle	Colorless, needle
Crystal system	tricilinic	tricilinic	tricilinic
a, Å	11.2545 (10)	10.8986 (5)	13.1111 (7)
b, Å	18.0672 (18)	17.3609 (8)	16.1465 (7)
с, Å	20.425 (2)	19.6353 (9)	16.9214 (9)
a, deg	114.844 (3)	83.290 (2)	75.200 (4)
β, deg	101.984 (3)	83.085 (2)	85.670 (4)
γ, deg	90.435 (3)	83.055 (2)	75.891 (4)
V, \hat{A}^3	3665.7 (6)	3641.3 (3)	3358.57
ho calc, g/cm ³	1.263	1.267	1.267
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Z value	2	2	2
Temperature, K	200 (2)	200 (2)	140
no. of reflections measured	29441	6767	23601

Table S1. Crystallographic parameters of KR216 and spiro-OMeTAD.

no. of variables	930	904	909
Residuals: R; wR2	0.0982, 0.2480	0.0645, 0.1511	0.0419, 0.1068

The data of spiro-OMeTAD originated from $\ensuremath{\mathsf{EPFL}}^4$

2.3 Density functional theory (DFT) calculation

2.3.1 $\$ Calculated E_{HOMO}/E_{LUMO} energy levels



Fig S13. HOMO and LUMO of spiro-OMeTAD and spiro-type HTMs obtained from DFT

calculations

Table S2. Calculated E_{HOMO}/E_{LUMO} energy levels and Contribution of various parts to energy levels



UTM	ГМ Orbital Energy(eV)		Orbital component		
1111/01			1	2	X
spiro CN	НОМО	-4.41	22.5	73.6	3.8
spilo-en	LUMO	-2.41	56.8	3.4	39.8
conirco DS	НОМО	-4.34	25.2	71.3	3.5
spiro-r s	LUMO	-2.39	57.4	3.9	38.8
oning OMATAD	НОМО	-4.34	35.9	64.1	-
spiro-OmeTAD	LUMO	-0.76	76.2	23.8	-

2.3.2、Calculated ESP profiles



Fig S14. (a) Calculated ESP profiles of spiro-OMeTAD and spiro-type HTMs. (b) DFT-optimized structure of spiro-type HTMs.

2.4 Thermal properties



Fig S15. TGA curves of spiro-CN and spiro-PS.



Fig S16. DSC curves of spiro-CN and spiro-PS.

HTM	T _{dec} [°C]	T _m [°C]	T _g [°C]
spiro-CN	409	202,243	106
spiro-PS	348	181	91
spiro-OMeTAD	437	-	121

Table S3. Thermal properties of spiro-CN and spiro-PS

 T_{dec} is decomposition temperature determined from TGA (5% weight loss); T_m is melting temperature and T_g is glass transition temperature, determined from DSC. All experiments were performed under N_2 atmosphere. The data of spiro-OMeTAD originated from Seok's group.⁵

2.5 Surface morphology Characterization



Fig S17. (a) SEM images of different HTMs coating perovskite films. (b)Top-view AFM images of different HTMs thin films deposited on perovskite layer.

2.6 The hole mobility tested by SCLC

Table S4. Hole mobility of different HTMs

HTM	spiro-OMeTAD	spiro-CN	spiro-PS
$\mu(cm^2/Vs)$	4.71×10 ⁻⁴	1.04×10 ⁻³	3.48×10 ⁻³

2.7、 Statistical data of TRPL

Samples	$\tau_1(ns)$	$\tau_2(ns)$	A_1	A_2	$\tau_{avg}(ns)$

Table S5. Statistics of all parameters of TRPL

Perovskite	3.06	61.37	0.60	0.40	57.31
Perovskite/spiro-CN	3.16	31.18	0.89	0.11	18.56
Perovskite/spiro-PS	3.04	24.76	0.87	0.13	14.96
Perovskite/spiro-OMeTAD	2.48	24.76	0.86	0.14	16.27

2.8、 Cross sectional SEM image



Fig S18.Cross sectional SEM images of the planar p-i-n structured PSCs device with different HTMs,

scale bar 500 nm.

2.9, Electrical impedance spectroscopy



Figure S19. (a) Electrical impedance spectroscopy (EIS), Nyquist plot under 0.1 sun illumination, at the same bias 0.7 V, which is the magnified figure in the range of 0-6000 in x-Axis for Figure 6(b).
(b) Equivalent circuit model for the Nyquist plots. Rs: series resistance. R_{ct}:transfer/transport resistance. R_{rec}: resistance of interfacial recombination. C: capacitance.

Table S6 EIS derived series resistance (R_s), transport resistance (R_{ct}) and recombination resistance (R_{rec}) for the different devices under 10 mW cm⁻² illumination at applied voltages (0.7 V).

Samples	$R_{\rm s}\left(\Omega\right)$	$R_{ m ct}\left(\Omega ight)$	$R_{ m rec}(\Omega)$
spiro-CN	22.86	2577	22286
spiro-S	19.28	726.5	4537
spiro-OMeTAD	25.89	877	10908

2.10, Average photovoltaic parameters

Table S7 Average photovoltaic parameters for 14 devices with different HTMs

HTM	Voc (V)	J _{SC} (mA cm ⁻²)	FF(%)	PCE(%)	H _{index} (%)
spiro-CN	1.15±0.01	22.27±0.21	74.74±1.52	19.11±0.33	5.27±2.34
spiro-PS	1.05±0.04	22.19±0.23	70.42±2.11	16.41±0.90	15.97±6.63
spiro-OMeTAD	1.10±0.01	22.39±0.30	76.87±2.07	19.07±0.31	8.06±1.00

These statistical values are from reverse scan measurement except $H_{index}(\%)$ which is based on both forward and reverse scan measurement.

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