

Supplementary information

Novel spiro-based hole transporting materials for efficient perovskite solar cells

Ming-Hsien Li¹, Che-Wei Hsu², Po-Shen Shen¹, Hsin-Min Cheng¹, Yun Chi^{2*}, Peter Chen^{1,3,4**}, Tzung-Fang Guo^{1,3,4}

¹Department of Photonics, National Cheng Kung University, Tainan, Taiwan 701

²Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30013

³Research Center for Energy Technology and Strategy (RCETS)

⁴Advanced Optoelectronic Technology Center (AOTC)

*Corresponding author: ychi@mx.nthu.edu.tw

**Corresponding author: petercyc@mail.ncku.edu.tw

Experimental Section

General Procedures. All reactions were performed under nitrogen. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. All reactions were monitored by TLC with pre-coated silica gel plates (Merck, 0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV irradiation at 254 or 365 nm. Flash column chromatography was carried out using silica gel obtained from Merck (230 - 400 mesh). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ¹H NMR spectra were recorded on a Bruker-400 or INOVA-500 instrument; chemical shifts are quoted with respect to the internal standard tetramethylsilane. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

Synthesis of 2-bromo-N,N-bis(4-*t*-butylphenyl)aniline. A mixture of di(4-*t*-butylphenyl)amine (2.0 g, 7.1 mmol) and 1-bromo-2-iodobenzene (3.1 g, 10.6 mmol) was heated to 140°C for 12 h. After cooled to RT, the mixture was concentrated and the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over Na₂SO₄ and concentrated. The crude product was purified by SiO₂ column chromatography eluting with a 20:1 mixture of hexane and CH₂Cl₂ to obtain a white powder (1.1 g, 36%).

^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.89 (d, $J = 8$ Hz, 1 H), 7.34 (t, $J = 8$ Hz, 1 H), 7.22 (d, $J = 8.8$ Hz, 4 H), 6.94 (t, $J = 8$ Hz, 1 H), 6.86 (d, $J = 8.8$ Hz, 4 H), 1.28 (s, 18 H).

Synthesis of tri(4-*t*-butylphenyl)amine. To a 100 mL of reaction flask was added di-(4-*t*-butylphenyl)amine (5.0 g, 17.8 mmol), $\text{Pd}(\text{dba})_2$ (511 mg, 0.9 mmol), tri-*t*-butylphosphine (360 mg, 1.8 mmol), potassium *t*-butoxide (6.0 g, 53.4 mmol), 1-bromo-4-*t*-butylbenzene (7.9 g, 37.3 mmol) and toluene (50 mL). The mixture was refluxed for 12 h and then cooled to RT. Volatiles were removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was washed with methanol to afford white powder (5.21 g, 71.5%).

^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.20 (d, $J = 8.7$ Hz, 6 H), 6.98 (d, $J = 8.7$ Hz, 6 H), 1.27 (s, 27 H).

Synthesis of 2-bromo-4-*t*-butyl-*N,N*-bis(4-*t*-butylphenyl)aniline. Tri(4-*t*-butylphenyl)amine (500 mg, 1.2 mmol) was added to a 100 mL flask with 20 mL of CH_2Cl_2 . After 10 min, NBS (226 mg, 1.3 mmol) in 3.0 mL DMF was added dropwise. The solution was stirred at RT for 1 h. The product was precipitated by addition of ethanol, and recrystallized twice from CH_2Cl_2 /ethanol to afford colorless crystals (500 mg, 84%).

^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.61 (d, $J = 2.4$ Hz, 1 H), 7.31 (dd, $J = 8.3, 2.4$ Hz, 1 H), 7.22 (m, 5 H), 6.90 (d, $J = 6.8$ Hz, 4 H), 1.32 (s, 9 H), 1.29 (s, 18 H).

Synthesis of 2,7-bis(bis(4-methoxyphenyl)amino)-fluoren-9-one. To a round bottom flask was added 4,4'-dimethoxydiphenylamine (5.0 g, 21.8 mmol), $\text{Pd}(\text{dba})_2$ (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). The mixture was refluxed for 12 h, cooled to RT and then concentrated. The residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by SiO_2 column chromatography, eluting with a 1:4 mixture of ethyl acetate and hexane and then recrystallized in CH_2Cl_2 /hexane solution to obtain a dark-blue crystal (5.6 g, 84%).

^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.34 (d, $J = 8$ Hz, 2 H), 7.31 (d, $J = 8.4$, 8 H),

6.96 ~ 6.89 (m, 12 H), 3.80 (s, 12 H).

Synthesis of CW3. A solution of 2-bromophenyldiphenylamine (900 mg, 2.8 mmol) in dry THF (40 mL) was treated with *n*-BuLi (1.4 mL, 2.5 M in *n*-hexane) under nitrogen at -78 °C. After 30 min, a solution of 2,7-bis(bis(4-methoxyphenyl)amino)-fluoren-9-one (1.8 g, 2.8 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 30 min at -78 °C, and allowed to warm to RT. After 12 h, the solution was concentrated and the residue was extracted with CH₂Cl₂ and washed with brine and water in sequence. After dried over anhydrous Na₂SO₄ and concentrated under reduced pressure, the residue was washed with ethyl acetate and the tertiary alcohol intermediate was obtained as white powder.

Without further purification, the tertiary alcohol was added to a mixture of concentrated aqueous HCl (1.5 mL) and acetic anhydride (50 mL). After refluxed for 12 h, the reaction was quenched with ice water and neutralized with NaHCO_{3(aq)}. The crude product was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and purified by silica gel column chromatography, eluting with a 1:1 mixture of CH₂Cl₂ and hexane. The product was recrystallized with CH₂Cl₂/hexane as white crystals (2.1 g, 87%).

¹H NMR (400 MHz, DMSO, 298 K): δ 7.55 ~ 7.51 (m, 5 H), 6.96 ~ 6.93 (m, 10 H), 6.89 (s, 2 H), 6.82 (d, *J* = 8.8 Hz, 8 H), 6.74 ~ 6.68 (m, 6 H), 6.49 (d, *J* = 8 Hz, 2 H), 6.11 (d, *J* = 8 Hz, 2 H), 3.69 (s, 12 H). MS [FAB], *m/z* 862.2, M⁺. Anal. Calcd. for C₅₉H₄₇N₃O₄: C, 82.21; H, 5.50; N, 4.87. Found: C, 82.06; H, 5.33; N, 4.83.

Synthesis of CW4. Following the procedure described for **CW3** afforded a white powder of **CW4** (1.8 g, 63%)

¹H NMR (400 MHz, DMSO, 298 K): δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 8.4 Hz, 2 H), 7.12 (s, 2 H), 6.99 ~ 6.94 (m, 10 H), 6.83 ~ 6.79 (m, 10 H), 6.71 ~ 6.67 (m, 3 H), 6.62 ~ 6.59 (m, 2 H), 6.19 (d, *J* = 8.4 Hz, 1 H), 6.14 (d, *J* = 8.8 Hz, 1 H), 3.72 (s, 12 H), 1.43 (s, 9 H), 1.10 (s, 9 H). MS [FAB], *m/z* 974.2, M⁺. Anal. Calcd. for C₆₇H₆₃N₃O₄: C, 82.60; H, 6.52; N, 4.31. Found: C, 82.27; H, 6.35; N, 4.21.

Synthesis of CW5. Following the procedure described for **CW3** afforded a white crystal of **CW5** (1.6 g, 61%)

^1H NMR (400 MHz, DMSO, 298 K): δ 7.59 ~ 7.55 (m, 4 H), 7.16 (s, 2 H), 7.00 ~ 6.93 (m, 10 H), 6.86 ~ 6.79 (m, 10 H), 6.71 ~ 6.68 (m, 4 H), 6.14 (d, $J = 8$ Hz, 2 H), 3.73 (s, 12 H), 1.43 (s, 9 H), 1.09 (s, 18 H). MS [FAB], m/z 1030.3, M^+ . Anal. Calcd. for $\text{C}_{71}\text{H}_{71}\text{N}_3\text{O}_4$: C, 82.76; H, 6.95; N, 4.08. Found: C, 82.91; H, 6.92; N, 3.98.

Device fabrication.

The cleaned FTO glass substrate was coated with dense TiO_2 film (cp- TiO_2) via spray pyrolytic deposition of 0.068 M of titanium diisopropoxide bis(acetylacetonate) solution in ethanol. The commercially available TiO_2 paste (JGC 18NRT) was diluted in ethanol by a 1:7 weight ratio and was deposited on the substrates by spin coating to obtain the mesoporous TiO_2 (mp- TiO_2) layer of 100 nm. After sintered at 500 °C for 1 hr, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor was spun onto the mp- TiO_2 coated substrates by a two-step spin coating process with 1000 rpm and 5000 rpm for 10 s and 30 s, respectively. During the second step, addition of a few drops of toluene was needed to produce uniformly packed perovskite film and immediately dried at 110 °C for 10 min. The 50 wt.% of $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution was prepared by dissolving an equimolar of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 into the mixture of γ -butyrolactone (GBL) and dimethyl sulfoxide (DMSO) (6:4 in volume ratio). The hole-transporting layer was deposited by spin coating with 5000 rpm for 30 s. The 60 mM HTMs solution were prepared by dissolving HTMs in 1 mL of chlorobenzene, followed by addition of 28.8 μL of *t*-butylpyridine (tBP), 17.5 μL of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI) in acetonitrile (52 mg/100 μL), and cobalt dopant FK102 in acetonitrile (3, 6, 9, 12 mg/40 μL). Finally, 60 nm of gold film was thermally evaporated as back electrode.

Characterization

The J - V curves were measured (2401 Source Meter, Keithley) under simulated AM 1.5 irradiation at an intensity of 100 mW/cm^2 generated by xenon lamp simulator. Scan rate is set to be 5000 mV/s to minimize the hysteresis.¹ The active area of device was defined using metal sheet with 0.2 cm^2 . The IPCE measurement was performed using monochromator (Newport Cornerstone 260) under illumination of 300 W xenon lamp simulator (Newport). The light soaking measurement (Suntest CPS+(atlas)) was conducted under illumination of visible light ranging from 300 to 800 nm, with light intensity of 75 mW/cm^2 and exposure temperature of 60 °C

Table S1. Device parameters of PSCs fabricated using 60 mM of **CW4** and varied **FK102** doping concentration.

conc. of FK102	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
3 mM	1020	18.09	0.60	11.02
6 mM	1000	17.57	0.61	10.77
9 mM	1060	19.62	0.67	13.96
12 mM	1050	17.06	0.74	13.23

Table S2. Device parameters of PSCs fabricated using 9 mM of **FK102** and varied concentration of **CW4**.

conc. of CW4	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
60 mM	1050	18.96	0.68	13.62
80 mM	1040	17.21	0.67	12.06
100 mM	1000	18.06	0.51	9.24

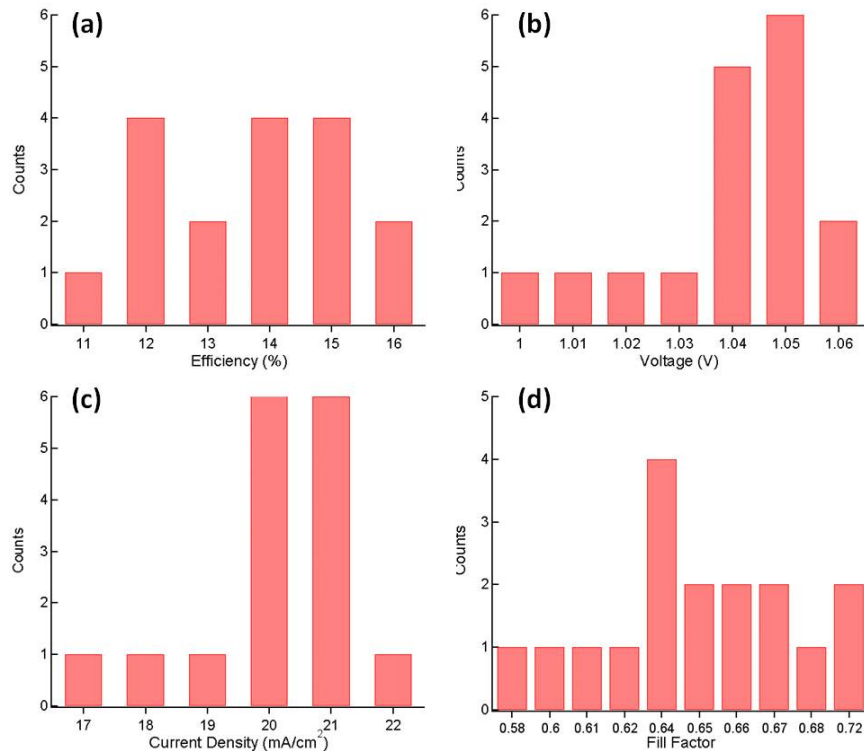


Figure S1. The statistic histograms of (a) PCE, (b) V_{OC} , (c) J_{SC} , and FF for the same batch of CW4-based perovskite solar cells.

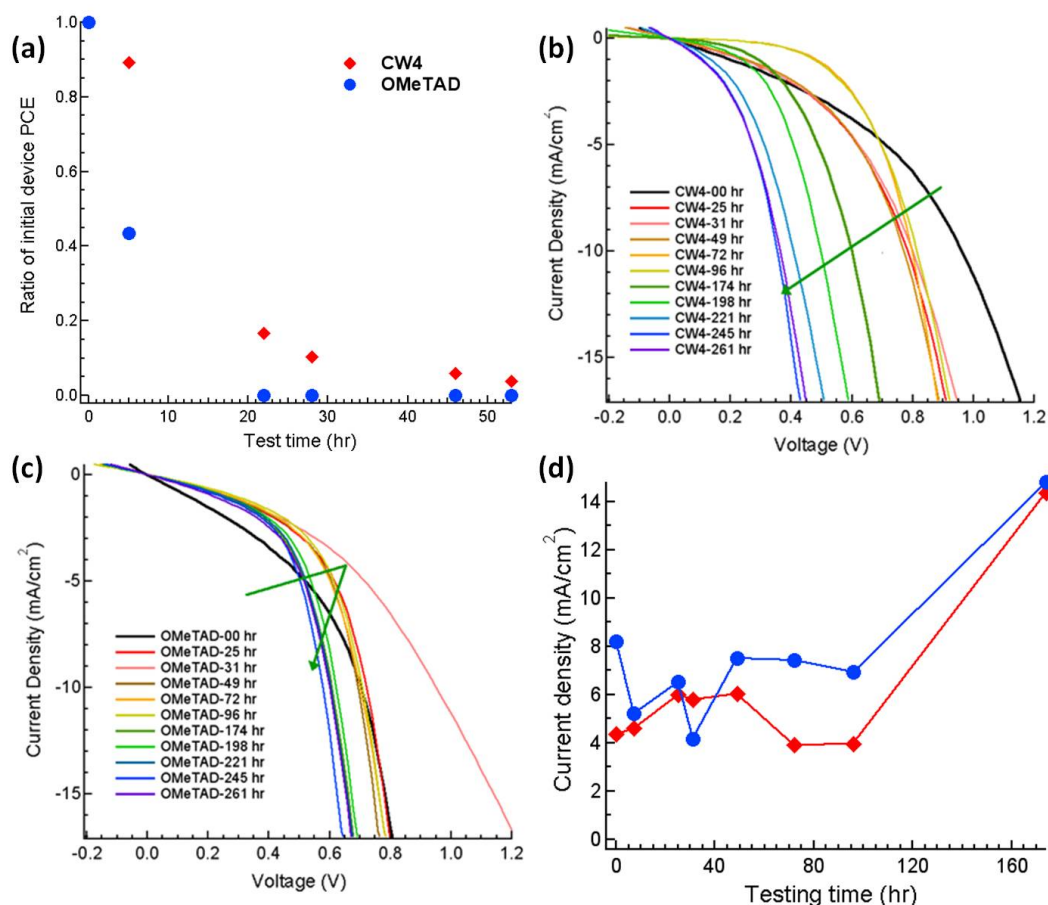


Figure S2. (a) Stability testing for normalized PCE of CW4 and spiro-OMeTAD devices; stability testing for J-V curves of (b) CW4 and (c) spiro-OMeTAD devices; (d) current density for both HTM close to the maximum power point of 0.66 V.

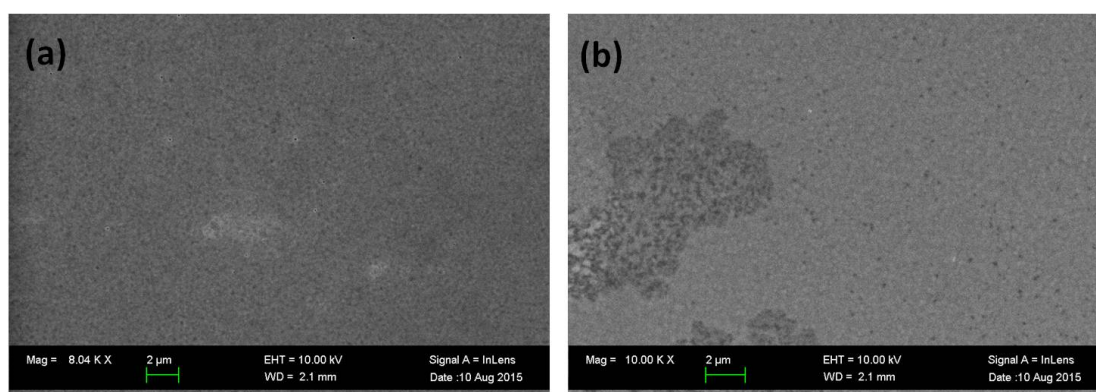


Figure S3. Surface morphology SEM images of (a) CW4 and (b) spiro-OMeTAD spin-coated on perovskite film.

References

1. W. Tress, N. Marinova, T. Moehl, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Gratzel, *Energy & Environmental Science*, 2015, **8**, 995.