SUPPORTING INFORMATION FOR

Supporting Information for:

Low-cost and LiTFSI-Free Diphenylamine-Substituted Hole Transporting Materials for Highly Efficient Perovskite Solar Cells and Modules

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Experimental Section

Materials

Synthesis of EH44

N-(2-ethylhexyl)-2,7-dibromocarbazole

2,7-Dibromocarbzole (2.00 g, 6.15 mmol) and K_2CO_3 (3.20 g, 23.19 mmol) were added to a dry Schlenk flask and purged with three cycles from vacuum to nitrogen to remove any moisture. Anhydrous N, N-dimethylformamide (DMF, 50 mL) was added, and the reaction was heated at 100 °C for 30 min. 1-Bromo-2-ethylhexane (1.10 mL, 6.15 mmol) was added in one portion, and the reaction was heated overnight. The mixture was poured into excess dichloromethane and extracted three times with deionized water. The organic portion was collected and dried over Na₂SO₄, and the solvent was removed by rotary evaporation. The crude solid was purified by column chromatography (silica gel, petroleum ether) to afford a white solid compound (2.50 g, 93%).

EH44

N-(2-ethylhexyl)-2,7-dibromocarbazole (1.76 g, 4 mmol), bis(4-methoxyphenyl) amine (2.3 g, 10 mmol), sodium t-butoxide (9.61 mg, 0.1 mmol), and bis(tri-t-butylphosphine) palladium (51.1 mg, 0.1 mmol) were added to a dry Schlenk flask and purged with three cycles from vacuum to nitrogen to remove any moisture. Anhydrous toluene (50 mL) was added via a syringe, and the reaction was heated at 110 °C for 24 h. The mixture was poured into excess dichloromethane and extracted three times with deionized water. The organic portion was collected and dried by Na₂SO₄, and the solvent was removed by rotary evaporation. The crude solid was purified by column chromatography (silica gel, petroleum ether/dichloromethane, v/v, 1:3) to afford **EH44** as a yellow solid compound (2.10 g, 72%). ¹HNMR (DMSO-d6, 500 MHz) δ (ppm): 7.76 (d, 2H,), 7.00 (d, 8H), 6.89 (d, 8H,), 6.79 (s, 2H), 6.67 (d, 2H,), 3.73 (d, 12H,), 1.54 (m, 1H), 1.04 (m, 8H), 0.72 (t, 3H,), 0.62 (t, 3H,).

EH44-ox

EH44 (0.73 g, 1 mmol) was dissolved in 50 mL dichloromethane in a 100 mL flask under N_2 and cooled to 0 °C with an ice bath. Silver bis(trifluoromethanesulfonyl)imide

(AgTFSI) (0.47 g, 1.2 mmol) was then added to the solution slowly and stirred in the absence of light under a constant N_2 flow for 24 h. The resultant silver precipitation was removed by filtration and the solution was dried by rotatory evaporation under vacuum to give a dark green powder. The powder was recrystallized from dichloromethane: diethyl ether=1:10 and dried under vacuum overnight (0.62 g, 61%).

Synthesis of SC-2

1-((2-ethylhexyl) oxy)-4-iodobenzene

A mixture of 4-iodophenol (2.20 g, 10.00 mmol), 1-bromo-2-ethylhexane (1.93 g, 10.00 mmol), K_2CO_3 (5.25 g, 38.00 mmol) and DMF (60 ml) was refluxed for 12 h. The mixture was poured into excess dichloromethane and extracted three times with deionized water. The organic portion was collected and dried over Na₂SO₄, and the solvent was removed by rotary evaporation. The crude solid was purified by column chromatography (silica gel, petroleum ether) to afford a white solid compound (3.10 g, 93%).

2,7-dibromo-9-(4-((2-ethylhexyl) oxy) phenyl)-9H-carbazole

A mixture of 1-((2-ethylhexyl) oxy)-4-iodobenzene (1.84 g, 5.54 mmol), 2,7-dibromo-9*H*-carbazole (1.50 g, 4.62 mmol), CuI (0.15 g, 0.79 mmol), 1,10-phenanthroline (0.09 g, 1.8 mmol), K_2CO_3 (2.4 g, 17.37 mmol) and DMF (60 ml) was refluxed for 24 h. The reaction was poured into excess dichloromethane and extracted three times with deionized water. The organic portion was collected and dried over Na₂SO₄, and the solvent was removed by rotary evaporation. The crude solid was purified by column chromatography (silica gel, petroleum ether/dichloromethane, v/v, 6:1) to afford a white fluid compound (1.80 g, 74%).

SC-2

2,7-Dibromo-9-(4-((2-ethylhexyl) oxy) phenyl)-9*H*-carbazole (1.68 g, 3.18 mmol), bis(4-methoxyphenyl) amine (1.60 g, 6.98 mmol), sodium t-butoxide (7.69 g, 0.08 mmol), and bis(tri-t-butylphosphine) palladium (40.88 mg, 0.08 mmol) were added to a dry Schlenk flask and purged with three cycles from vacuum to nitrogen to remove any moisture. Anhydrous toluene (30 mL) was added via a syringe, and the reaction was heated at 110 °C for 24 h. The mixture was into excess dichloromethane and

extracted three times with deionized water. The organic portion was collected and dried over Na₂SO₄, and the solvent was removed by rotary evaporation. The crude solid was purified by column chromatography (silica gel, petroleum ether/dichloromethane, v/v, 1:3) to afford SC-2 as a yellow solid compound (1.83 g, 70%).¹H NMR (500 MHz, d6-DMSO, 298 K), δ (ppm): 7.86(d, 2H), 7.28 (d, 2H), 7.00 (d, 2H), 6.95 (d, 8H), 6.85 (d, 8H), 6.72 (d, 2H), 6.67 (d, 2H), 3.86 (t, 2H,), 3.71 (s, 12H), 1.66 (m, 1H), 1.23-1.39 (m, 8H), 0.89 (d, 6H).¹³C NMR (126 MHz, d6-DMSO, 298 K), δ (ppm): (158.4, 155.6, 146.7, 142.5, 141.4, 129.4, 128.3, 126.1, 120.6, 117.6, 116.1, 115.6, 115.2, 102.1, 70.7, 55.7, 30.30, 28.9, 23.7, 23.0, 14.4, 11.4). HR-MS (ESI) m/z (%): [M]⁺, calcd for C₅₄H₅₅N₃O₅: 825.4142; found: 825.4116.

SC-2-ox

SC-2 (0.825 g, 1 mmol) was dissolved in 50 mL dichloromethane in a 100 mL flask under N₂ and cooled to 0 °C with an ice bath. Silver bis(trifluoromethanesulfonyl)imide (AgTFSI) (0.47 g, 1.2 mmol) was then slowly added to the solution and stirred in the absence of light under a constant N₂ flow for 24 h. The resultant silver precipitation was removed by filtration and the solution was dried by rotatory evaporation under vacuum to give a dark green powder. The powder was recrystallized from dichloromethane: diethyl ether=1:10 and dried under vacuum overnight (0.75 g, 68%).

Characterization:

¹H NMR was recorded on a Bruker Avance III HD 500 MHz spectrometer with DMSOd6 used as the solvent referenced to TMS (0 ppm). ¹³C NMR was recorded at 126 MHz in DMSO- d6 used as internal reference. Chemical shifts (δ) were given in ppm. HRMS was recorded on an Agilent 7250 mass spectrometry instrument. UV-Vis absorption spectra were provided by UV-vis spectrophotometer (lambda 750S, PerkinElmer). Cyclic voltammetry studies were conducted using an CHI600E system in a typical three-electrode cell with a glass carbon working electrode, a platinum wire counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode. The potentials were internally referenced with the ferrocene/ferricenium redox couple. The concentration of the analyte was between 0.5 and 1 mM with dry chlorobenzene as solvent under a nitrogen atmosphere. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was added at a concentration of 0.1 M as a supporting electrolyte. Thermogravimetric analysis and differential scanning calorimetry were performed on STA 449 F3 and TA-DSC2500 at a heating rate of 10 °C/min under nitrogen atmosphere respectively.

Device fabrication

FTO substrates preparation: The FTO glass is first etched with a femtosecond laser. Then ultrasonic cleaning was carried out for 20 minutes with dishwashing liquid, pure water, and ethanol, respectively. After drying with dry air, treat with ultraviolet ozone (UVO) for 15 minutes before use.

Electron transport layer (ETL) fabrication: SnO_2 was deposited onto clean FTO glass substrate by a chemical bath deposition (CBD) method according to reports. 5g urea was dissolved into 400 mL deionized water, followed by the addition of 100 µL mercaptoacetic acid and 5 mL HCl (37 wt.%), and then 1.096 g $SnCl_2 \cdot 2H_2O$ was dissolved in the solution (~ 0.012 M). The solution was stored in a fridge before use. The as-cleaned FTO glass was soaked into the diluted $SnCl_2 \cdot 2H_2O$ solution (~ 0.002 M) for 2.5 hours at 90 °C. Then it was washed by deionized water, dried by blowing air, and followed by the annealing at 180 °C for 1 hour. Before device fabrication, all the SnO_2 |FTO substrates were treated by UVO for 15 minutes. Further, perovskite and HTL deposition procedures were undertaken inside a N₂/Ar-filled glovebox.

Perovskite layer deposition: The $FA_{0.92}MA_{0.08}PbI_{2.76}Br_{0.24}$ perovskite solution (1.53 M PbI₂, 1.4 M FAI, 0.11 M MAPbBr₃, 0.5 M MACl in DMF: DMSO = 8:1 volume ratio) was spin coated at 1000 rpm for 10 s and 5000 rpm for 30 s onto the ETLs substrate. 10 s into the 5000rpm setting, 120 µL of ethyl acetate (EA) was deposited and the FTO|ETL|perovskite sample was heat treated at 100 °C for 60 min. For the fabrication of perovskite layer, the i-BABr isopropanol solution (~ 2.31 mg/mL) was prepared. Then 30µL solution was dropped on the perovskite layer, after spin-coating at the rate of 4000 r/min for 20 s and then heating at 100 °C for 5 min.

Hole transporting layer (HTL) deposition:

spiro-OMeTAD: The *spiro*-OMeTAD solution was prepared by dissolving 73 mg *spiro*-OMeTAD and 30 µL 4-tert-butylpyridine into 1 mL chlorobenzene followed by

adding 18 μ L of a stock solution of 520 mg/mL lithium bis-(trifluoromethylsulfonyl) imide in acetonitrile and 29 μ L FK209 (pre-dissolved as a 300 mg/mL stock solution in acetonitrile). 30 μ L of the *spiro*-OMeTAD solution was loaded onto the perovskite substrate and spin coated at 3000 rpm for 30 s with the ramp of 2000 rpm/sec.

EH44: The EH44 solution was prepared by dissolving 19.8 mg EH44 and 16.2 mg EH44-ox into 1 mL chlorobenzene followed by adding 30 μ L 4-tert-butylpyridine. 30 μ L of the EH44 solution was loaded onto the perovskite substrate and spin coated at 3000 rpm for 30 s with the ramp of 2000 rpm/sec.

SC-2: The SC-2 solution was prepared by dissolving 36.9 mg SC-2 and 5.7 mg SC-2ox into 1 mL chlorobenzene followed by adding 30 μ L 4-tert-butylpyridine. 30 μ L of the SC-2 solution was loaded onto the perovskite substrate and spin coated at 3000 rpm for 30 s with the ramp of 2000 rpm/sec.

Metal evaporation: 5 nm thick of MoO_X and 100 nm thick of Ag were deposited on HTL using thermal evaporation to complete the device fabrication.

Device characterization:

The perovskite and HTL films were investigated using field-emission scanning electron microscope (SEM) (S-4800, Hitachi, Japan), Ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi), UV-Vis spectrometer (lambda 750 S, PerkinElmer), X-ray diffractometer (XRD, D8 Advance). PL, TRPL, respectively. The current density-voltage (*J-V*) curves of these PSCs were measured using a Keithley 2400 source meter in the room environment. The light source was a solar simulator (Oriel 94023 A, 300 W) matching AM 1.5G. The intensity of the light was 100 mW cm⁻² calibrated by a standard silicon reference solar cell (Oriel, VLSI standards). The *J-V* scans were recorded at 100 mV/s from both forward (-0.1 V \rightarrow 1.2 V) and reverse (1.2 V \rightarrow -0.1 V) directions. All devices were tested using a black metal aperture with a defined active area of 0.16 cm² for the small devices.

The conductivity normalized to the device geometry was calculated according to the equation

$$\sigma = \frac{l}{V} \frac{d}{(2n-1)lh}$$

where I is the measured current, V is the applied voltage, d is the spacing between adjacent electrodes, n is the number of finger pairs, l is the length of the overlap area of the fingers, and h is the thickness of the HTM film. The thickness of the different doped sample was determined by cross-sectional SEM images and step profiler. All the devices are cooled down before each test.



Figure S1. (a) Synthesis routes of SC-2. (b) Reaction scheme for the HTMs-ox, used as the Li-free dopant in this study.



Figure S2. UV-Vis absorption and emission spectra of (a) EH44 and SC-2 films, and (b) *spiro*-OMeTAD film.



Figure S3. DSC spectra of EH44, SC-2, SC-2-ox doped SC-2 (15.5mol%), and SC-2-ox.



Figure S4. (a) Schematic illustration of the gold IDAs used for conductivity measurements. The distance between adjacent fingers is $d = 9.5 \,\mu\text{m}$, the length of the fingers is $l = 2 \,\text{mm}$, the number of finger pairs is 75. (b) *I-V* curves of *spiro*-OMeTAD, EH44, and SC-2 films. (c) *I-V* characteristics of SC-2 films doped with different molar ratio of SC-2-ox. (d) Conductivity derived from (c) as a function of SC-2-ox content.



Figure S5. Evolution of XRD patterns of FTO|SnO₂|FA_{0.92}MA_{0.08}PbI_{2.76}Br_{0.24} films, and covered with doped *spiro*-OMeTAD, doped EH44, and doped SC-2 HTLs.



Figure S6. Optical microscope images of (a) FA_{0.92}MA_{0.08}PbI_{2.76}Br_{0.24} perovskite, and perovskite covered with (b) doped *spiro*-OMeTAD, (c) doped EH44, (d) doped SC-2.



Figure S7. Cross-sectional SEM images of a solar cell based on doped *spiro*-OMeTAD.



Figure S8. *J-V* curves of FTO|SnO₂|perovskite|HTL|MoOx|Ag solar cell performance

with HTLs based on different molar ratio of SC-2-ox.



Figure S9. Statistics of the (a) V_{OC} , (b) J_{SC} , (c) FF for solar cells based on doped *spiro*-OMeTAD, doped EH44, and doped SC-2 HTLs, collected from the 15 devices for each type. The solar cell architecture is FTO|SnO₂| perovskite|HTL|MoOx|Ag.



Figure S10. FLIM image of FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15} perovskite covered with doped *spiro*-OMeTAD. The sample structure is glass|perovskite|HTL.



Figure S11. Stability of non-encapsulated perovskite solar cells for (a) V_{OC} , (b) J_{SC} and (c) FF. Four devices for each type were aged at ambient with a RH of $25 \pm 5\%$ and temperature of 25 ± 5 °C under dark for 1450 h (ISOS-D-1).



Figure S12. The microscope images of (a) doped *spiro*-OMeTAD, (b) doped SC-2 HTL films aged at a relative humidity of $75 \pm 5\%$ and temperature of 55 ± 5 °C. The sample structure is FTO|SnO₂|perovskite|HTL.



| Chemical name | Cost for 1 g of SC-2 | Price of chemical |
|--------------------------------|----------------------|-----------------------|
| | (\$) | (\$ g ⁻¹) |
| dibromocarbazole | 2.86 | |
| 1-bromoexane | 0.03 | |
| 4-iodophenol | 0.30 | |
| bis(4-methoxyphenyl) amine | 3.00 | |
| K ₂ CO ₃ | 0.03 | |
| CuI | 0.01 | |
| L-proline | 0.03 | |
| $Pd_2(dba)_3$ | 2.14 | |
| Dichloromethane | 1.30 | |
| Petroleum ether | 0.40 | |
| SC-2 | | 10.10 |
| spiro-OMeTAD | | 114.29 |

 Table S1. Summaries of synthetic cost for the SC-2 molecule.

| HTL | | $\frac{V_{\rm oc}}{(\rm V)}$ | J _{SC} (mA/cm ⁻²) | FF | PCE (%) |
|-----------------------------------|-------------------------------|------------------------------|---|-------------------|-------------------|
| | average ^b | 1.06 ± 0.02 | $\frac{21.9 \pm 0.3}{21.9 \pm 0.3}$ | 0.33 ± 0.02 | 7.8 ± 0.5 |
| <mark>0 mol.%</mark> – | <mark>best^c</mark> | 1.07 | <mark>22.4</mark> | <mark>0.35</mark> | <mark>8.3</mark> |
| 5.5 | average | $\underline{1.07\pm0.02}$ | 22.8 ± 0.4 | 0.61 ± 0.01 | 18.4 ± 0.5 |
| <u>5.5 mol.</u> - | best | <mark>1.10</mark> | <mark>23.2</mark> | <mark>0.63</mark> | <mark>15.9</mark> |
| 10.5 mol 9/ | average | $\underline{1.10\pm0.02}$ | 24.0 ± 0.7 | 0.73 ± 0.05 | 19.2 ± 0.8 |
| 10.3 moi.7 ₀ | best | <mark>1.10</mark> | <mark>24.3</mark> | <mark>0.75</mark> | <mark>20.2</mark> |
| $15.5 \text{ mol} \frac{96}{2}$ = | average | $\frac{1.09\pm0.02}{}$ | 24.2 ± 0.4 | 0.74 ± 0.02 | 19.3 ± 0.5 |
| 15.5 moi.70 | best | <mark>1.10</mark> | <mark>24.6</mark> | <mark>0.76</mark> | <mark>20.6</mark> |
| 20 5 10/ - | average | $\underline{1.04\pm0.02}$ | 24.4 ± 0.2 | 0.68 ± 0.04 | 17.4 ± 0.8 |
| 20.5 mol.% | best | 1.07 | <mark>24.4</mark> | <mark>0.75</mark> | <mark>19.8</mark> |
| 25.5 | average | 1.01 ± 0.03 | 23.9 ± 0.3 | 0.67 ± 0.05 | 16.4 ± 0.5 |
| 25.5 mol.% - | best | 1.03 | <mark>24.3</mark> | 0.72 | <mark>18.0</mark> |

Table S2. Photovoltaic parameters^a of PSCs based on different molar ratio of SC-2-ox under AM 1.5G 1-sun simulated irradiation (mask area: 0.16 cm²).

^a V_{OC} , J_{SC} , FF and PCE data were derived from the *J*-*V* curves in the scan direction of forward-bias (FB) to short-circuit (SC). ^b The average parameters are extracted from recording 5 independent devices of each type in the scan direction of FB to SC. ^c The best-performing devices recorded from FB to SC.

Table S3. Parameters used to fit the bi-exponential equation for TPRL curves for the $FA_{0.92}MA_{0.08}PbI_{2.76}Br_{0.24}$ perovskite deposited different doped HTL layers. The sample structure is glass slide| $FA_{0.92}MA_{0.08}PbI_{2.76}Br_{0.24}$ |HTLs, and they are encapsulated without exposure to air during the measurement. The average PL lifetime $\tau_{avg} = \sum \alpha i \tau i$, where $\alpha i = Ai\tau i / \sum Ai\tau i$.

| sample | A1 | τ_1 (ns) | A2 | τ_2 (ns) | τ (ns) |
|------------------------------------|------|---------------|------|---------------|-------------|
| perovskite | 28.1 | 345.0 | 71.9 | 1876.3 | 1773.9 |
| with doped <i>spiro</i> -OMeTAD | 23.9 | 16.4 | 76.1 | 98.2 | 94.1 |
| with doped EH44 | 15.4 | 29.7 | 84.6 | 171.1 | 166.8 |
| with doped SC-2 | 17.2 | 21.7 | 82.8 | 144.5 | 140.8 |



Figure S14¹ H NMR spectrum of compound EH44.



Figure S15 ¹H NMR spectrum of compound SC-2.



Figure S16¹³C NMR spectrum of compound SC-2.



Figure S17 High-resolution mass spectrum of compound SC-2.