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# **Supporting Information**

Multifunctional Poly-N-Vinylcarbazole Interlayer in Perovskite Solar Cells for High Stability and Efficiency: A Test with New Triazatruxene-Based Hole Transporting Materials

Pei-Yang Su, Li-Bo Huang, Jun-Min Liu,<sup>\*</sup> Li-Min Xiao, Yi-Fan Chen, Marcel Mayor, Dai-Bin Kuang, and Cheng-Yong Su <sup>\*</sup>

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# **Experimental details**

#### Materials

All reagents were obtained from commercial sources and used as received. Solvents were purified using MBRAUN MB SPS-800 system. Anhydrous solvents used in Suzuki coupling reaction were degassed by N<sub>2</sub> bubbling for 20 min. Poly-N-vinylcarbazole (PVK) was purchased from Sigma-Aldrich and the average molecular weight (Mw) is 1100000.

The detailed synthetic procedures of 2,7,12-tris(4-methoxyphenyl)-5, 10, 15triethtltriindole (**SP-11**) and 2,7,12-tris(N,N-bis(4-methoxyphenyl)aniline)-5, 10, 15triethtltriindole (**SP-12**) were provided in the supporting information (**Scheme S1**). 4bromo-N,N-bis(4-methoxyphenyl)aniline (**2**) and N,N'-bis(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioaborolan-2-yl)aniline (**3**),<sup>[1]</sup> 6-bromo-N-ethylisatine (**5**), 6-bromo-N-ethyloxindole (**6**), and 2,7,12-Tribromo-5,10,15-triethyltriindole (**2-Br-TAT**),<sup>[2]</sup> and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) tris (bis(trifluoromethyl sulfonyl)imide)) (**FK209**)<sup>[3]</sup> were prepared according to the procedures in the literatures.



Scheme S1. Synthesis of SP-11 and SP-12. a) CuI, KOH, 1,10-phenanthroline, toluene, 120 °C; b) KOAc, PdCl<sub>2</sub>(dppf), DMSO, 80 °C; c) EtI, K<sub>2</sub>CO<sub>3</sub>, DMF, 70 °C; d)

 $N_2H_4$ · $H_2O$ , reflux; e) POCl<sub>3</sub>, reflux; f) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-methoxylphenl)aniline,  $K_2CO_3$ , Pd(PPH<sub>3</sub>)<sub>4</sub>, THF, H<sub>2</sub>O, 85 °C; and g) *p*methoxybenzene boronic acid,  $K_2CO_3$ , PdCl<sub>2</sub>(dppf), toluene, MeOH, 80 °C.

# Synthesis of 2,7,12-tris(N,N-bis(4-methoxyphenyl)aniline)-5, 10, 15triethtltriindole (SP-11)

The mixture of 2-Br-TAT (666 mg, 1 mmol), 3 (1.725 g, 4 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (115.6 mg, 0.1 mmol) was added to a schlenk flask under nitrogen atmosphere, and then degassed THF (24 mL) and K<sub>2</sub>CO<sub>3</sub> (2M, 6 mL) was added. The reaction mixture was then stirred for 24 h at 85 °C under N<sub>2</sub>, after which it was cooled and evaporated to remove solvent under reduced pressure. The residue obtained was treated with water, and extracted with dichloromethane. The combined organic extract was dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated to afford the crude material which was further purified by silica-gel column chromatography using hexane and dichloromethane as the eluant (2:1, v/v) to give a light yellow solid (964 mg). Yield: 72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.35 (bs, 3H), 7.80 (s, 3H), 7.63 (d, J = 8.4Hz, 6H), 7.56 (d, J = 8.4 Hz, 3H), 7.14 (d, J = 8.8 Hz, 12H), 7.09 (d, J = 8.0 Hz, 6H), 6.88 (d, J = 8.8 Hz, 12H), 5.08 (bs, 6H), 3.83(s, 18H), 1.67 (t, J = 6.8 Hz, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 156.0, 155.8, 148.6, 147.9, 141.0, 140.8, 138.5, 132.9, 132.0, 131.8, 131.2, 130.4, 129.4, 127.5, 127.4, 127.3, 127.2, 126.9, 126.7, 126.5, 126.1, 120.9, 120.6, 114.8, 114.7, 55.5, 33.4, 29.7, 26.9; MALDI-TOF: m/z 1339.74 ( $[M]^+$ ); Elemental analysis calcd (%) for C<sub>90</sub>H<sub>78</sub>N<sub>6</sub>O<sub>6</sub>: C, 80.69; H, 5.87; N, 6.27; Found: C, 80.63; H, 5.79; N, 6.31.

# Synthesis of 2,7,12-tris(4-methoxyphenyl)-5, 10, 15-triethtltriindole (SP-12)

The mixture of 2-Br-TAT (666 mg, 1 mmol),  $K_2CO_3$  (691 mg, 5 mmol), pmethoxybenzene boronic acid (608 mg, 4 mmol), and  $PdCl_2(dppf)$  (73.2 mg, 0.1 mmol) was added to a schlenk flask under nitrogen atmosphere, and then degassed toluene (10 mL) and MeOH (5 mL) was added. The reaction mixture was then refluxed over night under N<sub>2</sub>, after which it was cooled and evaporated to remove solvent under reduced pressure. The residue obtained was treated with water, and extracted with dichloromethane. The combined organic extract was dried over anhydrous MgSO<sub>4</sub>, filtered, and evaporated to afford the crude material which was further purified by silica-gel column chromatography using hexane and dichloromethane as the eluant (3:2, v/v) to give a yellow solid (643 mg). Yield: 86%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.37 (d, *J* = 8.4 Hz, 3H), 7.80 (s, 3H), 7.74 (d, *J* = 8.4 Hz, 6H), 7.57 (d, *J* = 8.0 Hz, 3H), 7.07 (d, *J* = 8.4 Hz, 6H), 5.10 (q, *J* = 6.4 Hz, 6H), 3.91 (s, 9H), 1.68 (t, *J* = 6.8 Hz, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 159.0, 141.4, 138.8, 135.9 134.5, 130.9, 128.8, 128.4, 122.2, 121.7, 119.1, 114.3, 108.2, 65.6, 55.4, 41.6, 31.6, 30.6, 29.3, 22.7, 19.2, 15.7, 14.1, 13.7; MALDI-TOF: m/z 747.21 ([M]<sup>+</sup>); Elemental analysis calcd (%) for C<sub>51</sub>H<sub>45</sub>N<sub>3</sub>O<sub>3</sub>: C, 81.90; H, 6.06; N, 5.62; Found: C, 81.80; H, 6.12; N, 5.61.

#### **Compound Characterization**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a BRUKER 400 MHz spectrometer. Mass spectral data were obtained on an ultrafleX-treme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 240C elemental analyzer. The absorption spectra of the HTMs in solution were observed with a Shimadzu UV-2450 spectrometer and fluorescence spectra were measured with a Hitachi F-4500 spectrometer. Cyclic voltammograms (CV) were recorded using a CHI 832 electrochemical analyzer with platinum plate as working electrode, Ag/AgCl as reference electrode, Pt wire as counter electrode. CVs were measured with 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte in DCM. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 800 °C with a heating rate of 10 °C min<sup>-1</sup> in the air.

# Ultraviolet photoelectron spectroscopy

The TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PVK and PVK layers were deposited onto cleaned ITO by spin-coating, respectively. UPS spectra were acquired from He I (21.22 eV) excitation lines using a ESCALAB 250 system (Thermo Fisher Scientific) at base pressure of  $5 \times 10^{-10}$  mbar. All experiments were calibrated to the Fermi edge of an atomically clean gold surface.

# Hole mobility measurement

For the SCLC hole-only diode devices, a poly(3,4-ethylenedioxythiophene): poly(styrene- sulfonate) (PEDOT:PSS) coated indium tin oxide (ITO) substrate was used to enable hole injection. The HTM layers were prepared by evaporation method. MoO<sub>3</sub>/Al was used as the top electrode which preferentially allows for hole collection and hinders electron injection.

#### **Fabrication of solar cells**

Optically transparent fluorine doped SnO<sub>2</sub> (FTO) conducting glass was purchased from Nippon Sheet Glass (15  $\Omega$ /square), Japan, and cleaned by a standard procedure.<sup>[4]</sup> FTO glass was etched with Zinc powder and aqueous HCl solution (2 M), and then cleaned with the deionized water, alcohol, and acetone successively by ultrasonication. A TiO<sub>2</sub> compact layer was prepared onto the FTO by spin-coating with TiO<sub>2</sub> nanocolloidal solution <sup>[5]</sup> at 3000 rpm for 60 s and then it was calcined at 500 °C for 1 h. After cooling to room temperature, the TiO<sub>2</sub>-coated FTO film was immersed in TiCl<sub>4</sub> aqueous solution (0.04 M) at 70 °C for 30 min and then heat-treated at 500 °C for 30 min. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> precursor solution (0.88 M PbCl<sub>2</sub> and 2.64 M CH<sub>3</sub>NH<sub>3</sub>I <sup>[6]</sup> dissolved in DMF) was deposited onto the TiO<sub>2</sub>-coated FTO film prepared above by spin-coating at 5000 rpm for 60 s, and dried on a hot plate at 95 °C for 2 h. The PVK was deposited on the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> film by spin-coating at 2000 rpm for 120s. The hole transport material (HTM) was deposited on the PVK/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> film by spin-coating at 5000 rpm for 60 s. The HTM solution was each prepared by dissolving **SP-11** (50 mg), **SP-12** (70 mg), or spiro-OMeTAD (72.5 mg) in 1 mL chlorobenzene, 28.8  $\mu$ L *tert*-butylpyridine (TBP) solution and 17.5  $\mu$ L lithium bis(trifluoro methylsulfonyl) imide (Li-TFSI)/acetonitrile (520 mg/mL). Co-dopant **FK209** was predissolved into acetonitrile and added into the HTM solution at ratios of 15 mol%. For the metal electrode, a 50 nm Au cathode layer was deposited by magnetron sputtering and an active area of 0.16 cm<sup>2</sup> was defined.<sup>[7]</sup>

#### **Device Characterization**

The current-density voltage (*J-V*) curves of PSCs were recorded by using a Keithley 2400 source meter under illumination of one sun AM 1.5 G (100 mW cm<sup>-2</sup>) with a solar light simulator (Oriel, Model:91192),<sup>[8]</sup> which was calibrated with a NREL standard Si solar cell. The incident photon-to-current conversion efficiencies (IPCEs) were measured on a Keithley 2000 multimeter as a function of wavelength from 380 to 850 nm on the basis of a Spectral Products DK240 monochromator.

Powder X-ray diffraction (XRD) were recorded on a Bruker D8 Advance X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Photoluminescence (PL) (excitation at 406 nm) and time-resolved photoluminescence (TRPL) (excitation at 406 nm and emission at 785 nm) were measured with Edinburgh Instruments LTD (FLSP920). Contact angles were determined by contact angle system from Dataphysics (OCA20). The morphologies of the prepared films were examined by field-emission scanning electron microscope (FE-SEM, Hitachi S4300).

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**Figure S1.** SEM images of PVK films deposited on a perovskite layer, from a range of PVK concentrations: (a) 4, (b) 8, (c) 12, (d) 16 mg/mL, and (e) pure perovskite film.



**Figure S2.** (a) Photographs and (b-e) XRD patterns illustrating the visible degradation of the perovskite layers under various conditions.



**Figure S3.** (a) Photoluminescence (PL) spectra (excitation at 406 nm) and (b) timeresolved photoluminescence (TR-PL) (excitation at 406 nm and emission at 785 nm) of bare perovskite film and perovskite films coated with PVK interlayer at various concentrations between perovskite and spiro-OMeTAD films.

Sample	$\tau_1$ (ns)	frac. 1	$\tau_2$ (ns)	frac. 2	ave. (ns)
Perovskite	22.1	9.9%	138.0	90.1%	126.5
Perovskite+spiro-OMeTAD	12.8	75.9%	79.5	24.1%	28.9
Perovskite+PVK4+spiro-OMeTAD	1.2	4.5%	20.9	95.5%	20.0
Perovskite+PVK8+spiro-OMeTAD	1.0	5.3%	16.9	94.7%	16.1
Perovskite+PVK12+spiro-OMeTAD	1.2	6.1%	17.3	93.9%	16.3
Perovskite+PVK16+spiro-OMeTAD	1.6	7.0%	19.7	93.0%	18.5

Table S1 Time-resolved PL measurements from Figure S3



**Figure S4.** UPS spectra of the perovskite film, perovskite/PVK layer, and PVK film in the cutoff (a) and onset regions (b).



**Figure S5.** Thermogravimetric analysis of **SP-11** and **SP-12** in comparison with spiro-OMeTAD.



Figure S6. Differential scanning calorimetry (DSC) curves of SP-11 and SP-12.



Figure S7. Absorption and emission spectra of SP-11 and SP-12 in  $CH_2Cl_2$  in comparison with spiro-OMeTAD.



**Figure S8.** Distribution of HOMO and LUMO levels for **SP-11** and **SP-12** as calculated with DFT on the B3LYP/6-31G\* level.



Figure S9. CV spectra of SP-11, SP-12 and spiro-OMeTAD.



**Figure S10.** (a) Steady state photoluminescence (PL) spectra (excitation at 406 nm) and (b) time-resolved photoluminescence (TRPL) (excitation at 406 nm and emission at 785 nm) of bare perovskite film and perovskite films containing PVK and different HTMs.

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Sample	$\tau_1$ (ns)	frac. 1	$\tau_2$ (ns)	frac. 2	ave. (ns)
perovskite	22.1	9.9%	138.0	90.1%	126.5
perovskite+spiro-OMeTAD	12.8	75.9%	79.5	24.1%	28.9
Perovskite+SP-11	22.7	71.4%	2.4	28.6%	16.9
Perovskite+SP-12	21.5	67.1%	2.5	32.5%	15.2

Table S2 Time-resolved PL measurements from Figure S9



Figure S11. Current density vs. voltage curves of perovskite solar cells with SP-11, SP-12 and spiro-OMeTAD as HTMs in absence (a) or presence (c) of PVK interlayer (c), and IPCE spectra of perovskite solar cells with SP-11, SP-12 and spiro-OMeTAD HTMs in absence (b) or presence (d) of PVK interlayers.

HTM	Scan	PVK	$J_{ m sc}$	V <sub>oc</sub>	FF	η (%)
	direction	(mg/mL)	$(mA/cm^2)$	(mV)		
spiro-OMeTAD	FB to SC	0	20.6	958	0.71	14.1
SP-11	FB to SC	0	19.8	978	0.72	13.9
SP-12	FB to SC	0	21.4	1000	0.73	15.5
spiro-OMeTAD	FB to SC	o	21.6	1016	0.77	16.9
	SC to FB	8	21.5	981	0.71	15.0
SP-11	FB to SC	o	22.3	1030	0.74	16.9
	SC to FB	0	22.2	1008	0.67	15.0
SP-12	FB to SC	0	22.8	1075	0.77	18.8
	SC to FB	8	22.8	1043	0.70	16.7

Table S3 Solar cell performance parameters extracted from Figure S10



**Figure S12.** Histograms of each value of a)  $J_{SC}$ , b)  $V_{OC}$ , c) *FF* and d) *PCE* for 20 **SP-12**-based perovskite solar cells.





**Figure S13.** IPCE of devices employing **SP-11** (a), **SP-12** (b) and spiro-OMeTAD (c) as HTMs and corresponding integrated short-circuit photocurrent densities.



Figure S14. The aging test for devices with SP-12 and spiro-OMeTAD as HTMs in presence and absence of PVK interlayer.