Supplementary information for:

Branched methoxydiphenylamine-substituted fluorene derivatives as hole transporting materials for high-performance perovskite solar cells

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General methods and materials

Chemicals were purchased from Sigma-Aldrich and TCI Europe and used as received without further purification. Chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (XPhos Pd G2) catalyst was purchased from Sigma-Aldrich. The ^{1}H and ^{13}C NMR spectra were taken on Bruker Avance III 400 (400 MHz) and Bruker Avance III 700 (700 MHz) spectrometers at RT. All the data are given as chemical shifts in δ (ppm). The course of the reactions products were monitored by TLC on ALUGRAM SIL G/UV254 plates and developed with I_2 or UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyser, Model 440 C/H/N/. Differential scanning calorimetry (DSC) was performed on a Q10 calorimeter (TA

Instruments) at a scan rate of 10 K min^{-1} in the nitrogen atmosphere. The glass transition temperatures for the investigated compounds were determined during the second heating scan. Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyser (TA Instruments) at a scan rate of 10 K min^{-1} in the nitrogen atmosphere. UV/Vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Microcells with an internal width of 1 mm were used. Melting points of the crystalline materials were determined using Electrothermal Mel-Temp DigiMelt MPA 161 melting point apparatus.

Cyclic voltammetry measurements

Electrochemical studies were carried out by a three-electrode assembly cell and potentiostat-galvanostat from Bio-Logic SAS. Measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and Pt wire as the reference electrode, and a Pt wire counter electrode at a scan rate 50 mV s^{-1}. Each measurement was calibrated with ferrocene (Fc).

Ionization Potential Measurements

The solid state ionization potential (I_p) of the layers of the synthesized compounds was measured by the electron photoemission in air method [1–3]. The samples for the ionization potential measurement were prepared by dissolving materials in $CHCl_3$ and were coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5-1 μm. Usually photoemission experiments are carried out in vacuum and high vacuum is one of the main requirements for these measurements. If vacuum is not high enough the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stable enough to oxygen and the measurements may be carried out in the air. The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2\text{-}5)\cdot10^{-8}$ W. The negative voltage of –300 V was supplied to the sample substrate. The counter-electrode with the 4.5×15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. The 10^{-15} – 10^{-12} A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy hν. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and $h\nu$ near the threshold [2, 3]. The linear part of this dependence was extrapolated to the hν axis and I_p value was determined as the photon energy at the interception point.

Hole Drift Mobility Measurements

The samples for the hole mobility measurements were prepared by spin-coating the solutions of the synthesized compounds on the polyester films with conductive Al layer. The layer thickness was in the range of 5-10 μm. The hole drift mobility was measured by xerographic time of flight technique (XTOF) [4–6]. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1-5 % of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in double logarithmic scale. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, U_0 – the surface potential at the moment of illumination.

Conductivity of thin organic films

Solutions of V852, V859 and V862 with molar concentrations of 40mM in chlorobenzene were prepared in an Argon filled glovebox They were spin-coated onto two OFET substrates (Fraunhofer IPMS) at 4000 rpm for 20 s inside the same glovebox. For the conductivity measurement, prior to deposition, the solution was doped with 5 mol% FK-209.

The conductivity measurement was done on a 2.5µm channel (by length). The channel width was 10mm and the channel height was 40nm.

The data were recorded with a Keithley 2612A by sweeping from -10 to 10 V (Source-drain voltage) at a scan rate of 1 V s^{-1}. The conductivity was calculated from linear fit (Ohm's law).

Device characterisation

Substrate preparation and Li-doping TiO_2

Nippon Sheet Glass 10 Ω/sq was cleaned by sonication in 2% Hellmanex water solution for 30 min. After rinsing with deionised water and ethanol, the substrates were further cleaned with UV ozone treatment for 15 min. Then, 30 nm TiO_2 compact layer was deposited on FTO via spray pyrolysis at 450 °C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. After the spraying, the substrates were left at 450 °C for 45 min and left to cool down to room temperature. Then, mesoporous TiO_2 layer was deposited by spin coating for 20 s at 4000 rpm with a ramp of 2000 rpm s^{-1}, using 30 nm particle paste (Dyesol 30 NR-D) diluted in ethanol to achieve 150-200 nm thick layer. After the spin coating, the substrates were immediately dried at 100 °C for 10 min and then sintered again at 450 °C for 30 min under dry air flow.

Li-doping of mesoporous TiO_2 is accomplished by spin coating a 0.1 M solution of Li-TFSI in acetonitrile at 3000 rpm for 30 s followed by another sintering step at 450 °C for 30 min. After cooling down to 150 °C the substrates were immediately transferred in a nitrogen atmosphere glove box for depositing the perovskite films.

Perovskite precursor solution and film preparation

The "mixed perovskite" precursor solution contained FAI (1 M), PbI_2 (1.1 M), MABr (0.2 M) and $PbBr_2$ (0.2 M) dissolved in anhydrous DMF:DMSO 4:1 (v:v). The perovskite solution was spin coated in a two steps program at 1000 and 6000 rpm for 10 and 30 s respectively. During the second step, 100 μL of chlorobenzene was poured on the spinning substrate 15 s prior to the end of the program. The substrates were then annealed at 100 °C for 1 h in a nitrogen filled glove box.

Hole transporting layer and top electrode

After the perovskite annealing, the substrates were cooled down for few minutes the respective HTM spiro-OMeTAD, V852, V859 and V862 were dissolved in chlorobenzene for a 70mM solution which was spin coated at 4000 rpm for 20 s. All HTMs were doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)- cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209, Dynamo) and 4-tert-Butylpyridine (TBP, Sigma-Aldrich). The molar ratio of additives for the HTMs weas: 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and TBP respectively.

Finally, 70-80 nm of gold top electrode was thermally evaporated under high vacuum.

Photovoltaic device testing

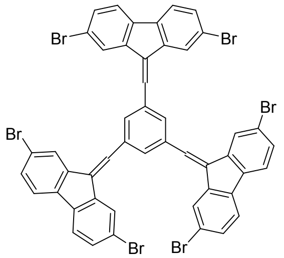
The solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott), and it was recorded during each measurement. Current-voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate was 10 mV s^{-1} and no device preconditioning, such as light soaking or forward voltage bias applied for long time, was applied before starting the measurement. The starting voltage was determined as the potential at which the cells furnish 1 mA in forward bias, no equilibration time was used. The cells were masked with a black metal mask (0.16 cm^2) to fix the active area and reduce the influence of the scattered light.

Table S1. Short circuit current-density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) of the best performing spiro-OMeTAD, **V852, V859, and V862** and devices on mixed perovskite. The curves were recorded at a scanning rate of 10 mV s^{-1} from forward bias (FB) to the short circuit condition (SC), and the other way around. Devices were masked with a metal aperture of 0.16 cm^2 to define the active area. No device preconditioning, such as light soaking or forward voltage bias applied for long time, was applied before starting the measurement.

HTM	**Scan direction**	**J_{sc} (mA cm^{-2})**	**V_{oc} (mV)**	**FF**	**PCE (%)**	**Light Intensity (mW cm^{-2})**
spiro	FB to SC	**22.3**	**1117**	**0.73**	**18.25**	**99.6**
	SC to FB	**22.3**	**1096**	**0.74**	**18.24**	
V852	FB to SC	**21.7**	**1139**	**0.71**	**17.74**	**98.7**
	SC to FB	**21.7**	**1135**	**0.71**	**17.77**	
V859	FB to SC	**23.3**	**1122**	**0.71**	**18.38**	**98.4**
	SC to FB	**23.3**	**1120**	**0.75**	**19.47**	
V862	FB to SC	**22.5**	**1140**	**0.76**	**19.58**	**99.6**
	SC to FB	**22.5**	**1139**	**0.77**	**19.96**	

The detailed synthetic procedures:

9,9',9''-(benzene-1,3,5-triyltrimethylylidene)tris(2,7-dibromo-9*H*-fluorene) (1)



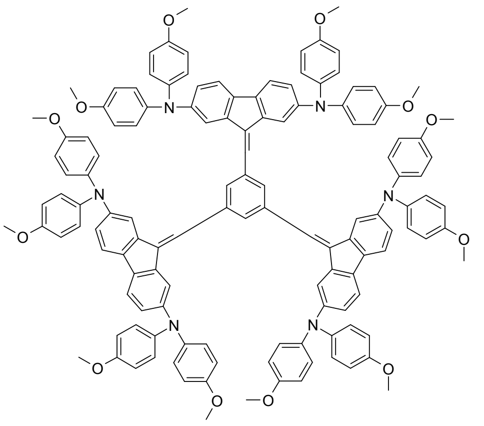
Aqueous 40% NaOH solution (21 mL) was added to a solution of benzene-1,3,5-tricarboxaldehyde (0.49 g, 3.0 mmol), 2,7-dibromofluorene (3.65 g, 11.27 mmol) and tetrabutylammonium bromide (0.52 g, 1.61 mmol) in toluene (21 mL) and the obtained mixture was stirred at room temperature for 2 hours. Formed precipitate was filtered off and washed with water and twice with ethanol to give the compound **1** as yellow powder (2.23 g, 68 %).

^{1}H NMR (700 MHz, DMSO-d_6): δ = 7.85 (d, J = 1.8 Hz, 3H), 7.84 (d, J = 1.8 Hz, 5H), 7.83-7.79 (m, 11H), 7.76 (d, J = 1.8 Hz, 5H);

^{13}C NMR (176 MHz, DMSO-d_6): δ = 145.88, 142.56, 139.81, 138.27, 135.24, 130.31, 128.71, 127.37, 123.99, 123.07, 122.59, 120.76.

Anal. calcd for $C_{48}H_{24}Br_6$: C, 53.38; H, 2.24; found: C, 53.58; H, 2.33.

9,9',9''-(benzene-1,3,5-triyltrimethylylidene)tris[*N*,*N*,*N*',*N*'-tetrakis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine] (V852)



A solution of **1** (1.08 g, 1.0 mmol), 4,4'-dimethoxydiphenylamine (2.06 g, 9.0 mmol) in dry 1,4-dioxane (17 mL) was purged with argon for 30 minutes. Afterwards, XPhos Pd G2 (0.024 g, 0.03

mmol) and sodium *tert*-butoxide (0.86 g, 9.0 mmol) were added and the solution was heated at reflux for 5 hours under Ar atmosphere. After cooling to room temperature, reaction mixture was filtered through celite, 35 mL of distilled water were added and extraction was done with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered, and solvent evaporated. The crude product was purified by column chromatography using 7:18 v/v THF/*n*-hexane as an eluent to collect **V852** as a light brown red solid (0.98 g, 50 %).

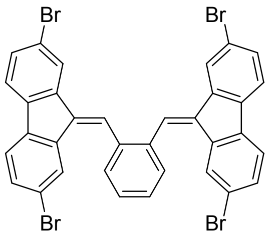
^{1}H NMR (700 MHz, DMSO-d_6): δ = 7.49 (t, *J* = 8.3 Hz, 6H), 7.24 (s, 3H), 7.12 (s, 3H), 7.07-7.01 (m, 15H), 6.98 (s, 3H), 6.90-6.83 (m, 15H), 6.73-6.69 (m, 3H), 6.61 (d, *J* = 8.8 Hz, 12H), 6.49 (d, *J* = 9.0 Hz, 12H), 3.61 (s, 18H), 3.52 (s, 18H);

^{13}C NMR (176 MHz, DMSO-d_6): δ = 155.94, 155.81, 147.84, 146.95, 141.08, 140.42, 137.32, 136.47, 136.19, 134.50, 132.54, 128.61, 126.67, 126.60, 121.69, 120.33, 120.18, 115.38, 114.92, 113.11, 55.57, 55.41.

Anal. calcd for $C_{132}H_{108}N_6O_{12}$: C, 80.47; H, 5.52, N, 4.27; found: C, 80.58; H, 5.66; N, 4.10.

$C_{132}H_{108}N_6O_{12}$ [M$^+$] exact mass = 1968.80, MS (ESI) = 1968.80, 1969.80, 1970.81, 1972.81, 1973.81.

9,9'-(benzene-1,2-diyldimethylylidene)bis(2,7-dibromo-9*H*-fluorene) (2)



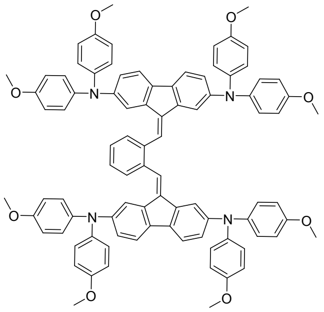
Aqueous 40% NaOH solution (18 mL) was added to a solution of phthaldialdehyde (0.5 g, 3.73 mmol), 2,7-dibromofluorene (3.02, g 9.32 mmol) and tetrabutylammonium bromide (0.43 g, 1.34 mmol) in toluene (18 mL) and the obtained mixture was heated at reflux for 1 h. Mixture was allowed to cool to room temperature and formed precipitate was filtered off and washed with water, ethanol and ethyl acetate to isolate the compound **2** as slightly yellow powder (1.67 g, 60 %).

^{1}H NMR (700 MHz, THF-d_8): δ = 7.63 (s, 2H), 7.20-7.10 (m, 7H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.99-6.92 (m, 8H);

^{13}C NMR (176 MHz, THF-d_8): δ = 120.65, 120.84, 121.28, 121.45, 121.85, 122.47, 126.27, 127.99, 129.13, 130.39, 130.62, 131.16, 132.28, 132.63, 134.15, 139.88, 140.42, 143.53, 145.03.

Anal. calcd for $C_{34}H_{18}Br_4$: C, 54.73; H, 2.43; found: C, 54.95; H, 2.33.

9,9'-(benzene-1,2-diyldimethylylidene)bis[*N*,*N*,*N*',*N*'-tetrakis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine] (V859)



A solution of **2** (0.45 g, 0.60 mmol), 4,4'-dimethoxydiphenylamine (0.83 g, 3.6 mmol) in anhydrous 1,4-dioxane (12 mL) was purged with argon for 30 minutes. Afterwards, XPhos Pd G2 (0.008 g, 0.01 mmol) and sodium *tert*-butoxide (0.35 g, 3.60 mmol) were added and the solution was heated at reflux for 5 hours under Ar atmosphere. After cooling to room temperature, reaction mixture was filtered through celite, 40 mL of distilled water were added and extraction was done with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered, and solvent evaporated. The crude product was purified by column chromatography using 1:20:29 v/v acetone/*n*-hexane/toluene as an eluent to collect **V859** as a light brown red solid (0.34 g, 48 %).

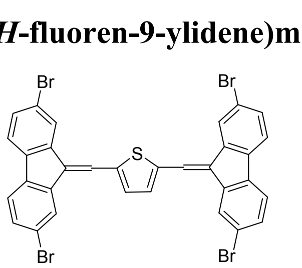
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 1H), 7.37 (d, *J* = 2.8 Hz, 2H), 7.35 (s, 1H), 7.20 (d, *J* = 2.0 Hz, 2H), 7.12 (s, 2H), 7.08-7.01 (m, 10H), 6.97-6.92 (m, 4H), 6.90-6.85 (m, 8H), 6.83-6.78 (m, 8H), 6.77-6.70 (m, 12H), 3.81 (s, 12H), 3.77 (s, 12H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.32, 147.12, 141.35, 141.22, 140.20, 137.59, 136.25, 134.93, 134.39, 133.06, 125.84, 125.79, 122.38, 121.75, 119.07, 118.45, 114.59, 114.47, 114.17, 55.41.

Anal. calcd for $C_{90}H_{74}N_4O_8$: C, 80.69; H, 5.57; N, 4.18; found: C, 80.52; H, 5.41; N, 4.29.

$C_{90}H_{74}N_4O_8$ [M$^+$] exact mass = 1338.55, MS (ESI) = 1338.55, 1339.55, 1340.55, 1341.56.

2,5-bis[(2,7-dibromo-9*H*-fluoren-9-ylidene)methyl]thiophene (3)



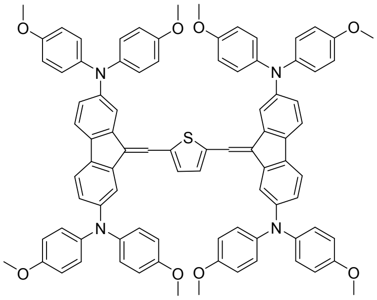
Aqueous 40% NaOH solution (15 mL) was added to a solution of 2,5-thiophenedicarboxaldehyde (0.42 g, 3.0 mmol), 2,7-dibromofluorene (2.43 g, 7.50 mmol) and tetrabutylammonium bromide (0.35 g, 1.09 mmol) in toluene (15 mL) and the obtained mixture was stirred at room temperature for 1 hour. Formed precipitate was filtered off and washed with water and ethanol to isolate the compound **3** as orange powder (1.55 g, 69%).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.76 (d, *J*=1.7 Hz, 4H), 7.67-7.66 (m, 1H), 7.62 (dd, *J* = 7.9, 1.8 Hz, 4H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.51-7.48 (m, 2H), 7.38 (d, *J* = 7.9 Hz, 4H);

^{13}C NMR (176 MHz, $CDCl_3$): δ = 142.29, 139.71, 137.48, 135.30, 130.15, 128.35, 127.87, 123.33, 121.86, 121.21.

Anal. calcd for $C_{32}H_{16}Br_4S$: C, 51.10; H, 2.14; found: C, 51.27; H, 2.30.

9,9'-(thiene-2,5-diyldimethylylidene)bis[*N*,*N*,*N*',*N*'-tetrakis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine] (V862)



A solution of **3** (0.75 g, 1.0 mmol), 4,4'-dimethoxydiphenylamine (1.38 g, 6.0 mmol) in anhydrous 1,4-dioxane (12 mL) was purged with argon for 30 minutes. Afterwards, XPhos Pd G2 (0.016 g, 0.02 mmol) and sodium *tert*-butoxide (0.58 g, 6.0 mmol) were added and the solution was heated at reflux for 5 hours under Ar atmosphere. After cooling to room temperature, reaction mixture was filtered through celite, 30 mL of distilled water were added and extraction was done with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered, and solvent evaporated. The crude product was purified by column chromatography using 3:22 v/v THF/*n*-hexane as an eluent to collect **V862** as a dark brown solid (0.68 g, 51%).

^{1}H NMR (700 MHz, DMSO-*d*$_6$): δ = 7.81 (s, 2H), 7.57 (s, 1H), 7.50 (t, *J* = 7.3 Hz), 7.42 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.28 (s, 1H), 7.02-6.93 (m, 10H), 6.90 (d, *J* = 8.8 Hz, 5H), 6.87-6.77 (m, 17H), 6.74 (d, *J* = 8.7 Hz, 5H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 9H), 3.71 (s, 9H), 3.52 (s, 6H);

^{13}C NMR (176 MHz, DMSO-*d*$_6$): δ = 156.16, 155.71, 155.59, 147.14, 141.39, 140.73, 140.40, 138.23, 134.35, 127.37, 126.20, 125.86, 123.95, 120.63, 118.93, 115.35, 55.67, 55.39.

Anal. calcd for $C_{88}H_{72}N_4O_8S$: C, 78.55; H, 5.39, N, 4.16; found: C, 78.39; H, 5.50; N, 4.00.

$C_{88}H_{72}N_4O_8S$ [M^+] exact mass = 1344.51, MS (MALDI-TOF) = 1344.26.

V859 and V862 cost calculations

The lab synthesis costs of **V859** and **V862** were estimated on the base of a model originally proposed by Osedach et al. [7]. Such a model has been recently applied by Petrus et al to the synthesis of other hole transporting materials [8].

For every synthetic step the actual amounts of reactants, catalysts, reagents, solvents and materials for workup and purification required to obtain 1 gram of **V859** and **V862** are reported (Tables S2, S3).

The price per kg of the commercially available chemicals and the cost per kg of the home-made intermediates were multiplied by the quantities that are required for the synthesis. The costs thus obtained were summed up affording an estimation of the direct material cost in analogy with what was reported in the literature [7, 8].

Table S2. Materials, quantities and cost for the synthesis of **V859**.

Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of chemical (€/kg)	Cost of chemical (€/g product)	Total cost (€/g)
Phthaldialdehyde	0.3			208	0.07	
2,7-Dibromofluorene	1.809			462	0.84	
Tetrabutylammonium bromide	0.259			422	0.11	
NaOH	4.467			4.28	0.02	
Toluene		15		2.46	0.04	
Ethanol			50	6.08	0.31	
Ethyl acetate			50	2.85	0.15	
9,9'-(benzene-1,2-diyldimethylylidene)bis(2,7-dibromo-9H-fluorene) (**2**)	6.835	15	100			1.54
9,9'-(benzene-1,2-diyldimethylylidene)bis(2,7-dibromo-9H-fluorene) (**2**)	1.160			1540	1.79	14.34
4,4'-Dimethoxydiphenylamine	2.139			1837.20	3.93	
XPhos Pd G2	0.012			31200	0.38	
Sodium *tert*-butoxide	0.897			200	0.18	
Anhydrous 1,4-Dioxane		15		71.20	1.07	
THF			50	8.88	0.45	
Ethyl acetate			100	2.85	0.29	
Na_2SO_4			5	6.08	0.04	
Acetone			20	1.52	0.04	
n-Hexane			400	3.16	1.27	
Toluene			580	2.46	1.43	
Silicagel			50	69.40	3.47	
V859	11.043	30	1205			14.34

14.34 €/g = 15.65 $/g

Table S3. Materials, quantities and cost for the synthesis of **V862**.

Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of chemical (€/kg)	Cost of chemical (€/g product)	Total cost (€/g)
2,5-thiophenedicarboxaldehyde	0.270			22100	5.97	
2,7-Dibromofluorene	1.094			462	0.51	
Tetrabutylammonium bromide	0.224			422	0.1	
NaOH	3.854			4.28	0.02	
Toluene		15		2.46	0.04	
Ethanol			50	6.08	0.31	
Ethyl acetate			50	2.85	0.15	
2,5-bis[(2,7-dibromo-9H-fluoren-9-ylidene)methyl]thiophene (3)	5.442	15	100			7.10
2,5-bis[(2,7-dibromo-9H-fluoren-9-ylidene)methyl]thiophene (**3**)	1.096			7100	7.79	
4,4'-Dimethoxydiphenylamine	2.005			1837.20	3.69	
XPhos Pd G2	0.011			31200	0.35	
Sodium *tert*-butoxide	0.840			200	0.17	
Anhydrous 1,4-Dioxane		15		71.20	1.07	
THF			170	8.88	1.51	
Ethyl acetate			100	2.85	0.29	
Na_2SO_4			5	6.08	0.04	
n-Hexane			880	3.16	2.79	
Silicagel			50	69.40	3.47	
V862	9.394	30	1205			21.17

21.17 €/g = 23.11 $/g

Table S4. Electrochemical properties of **V852, V859, V862**

Compound	E_{pc}^{ox} vs Fc (V)	E_{pa}^{ox} vs Fc (V)	$E_{1/2}$ vs Fc ^{a} (V)
V852	-0.06	-0.1	-0.08
V859	0	-0.06	-0.03
V862	0.08	-0.05	0.02

$^{a}E_{1/2}$= $(E_{pa}+E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

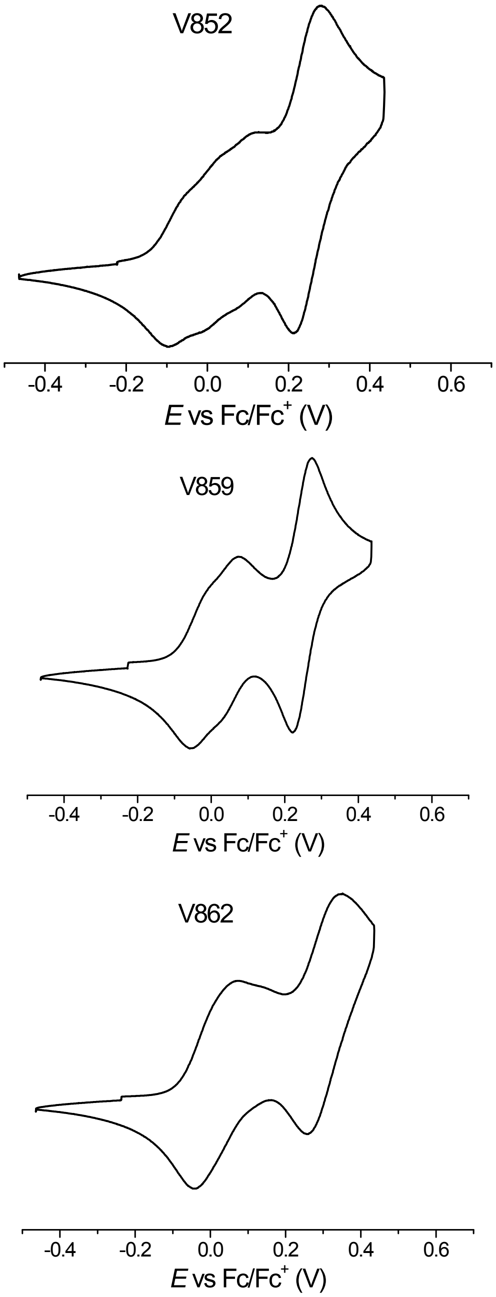


Figure S1. Oxidation waves of **V852, V859, V862** (scan rate = 50 mV·s^{-1}) in argon-purged dichloromethane solution.

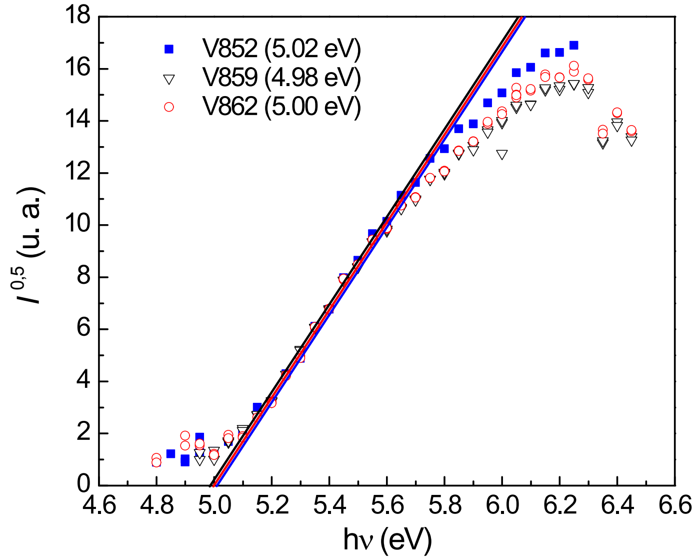


Figure S2. Photoemission-in-air spectra of **V852, V859, V862**.

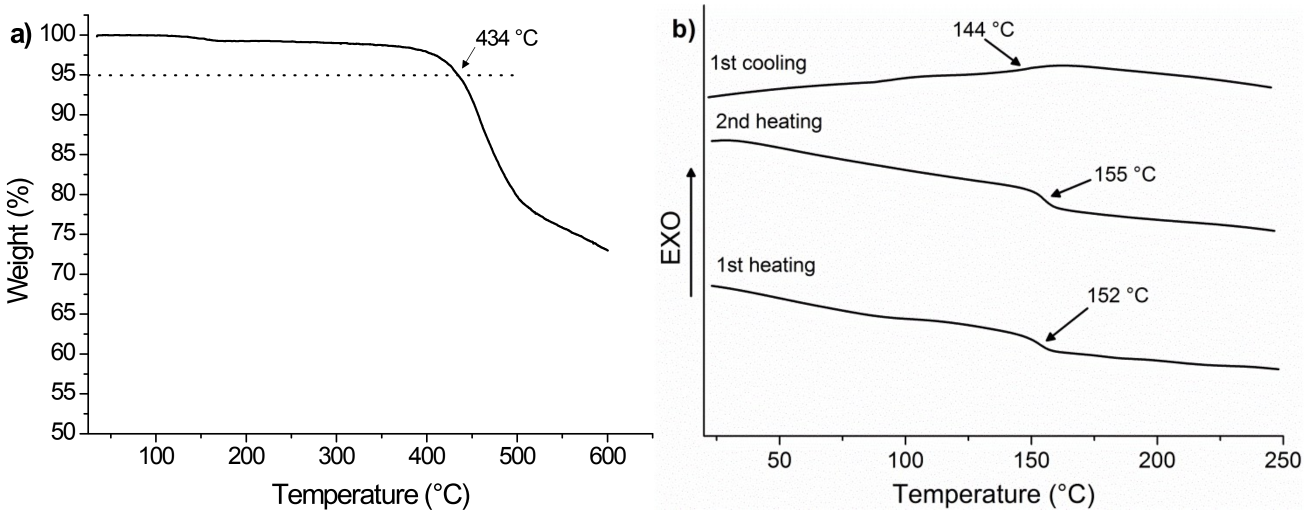


Figure S3. Thermogravimetric heating curve (a) and differential scanning calorimetry heating and cooling curves (b) of **V852** (heating/cooling rate 10 °K min^{-1}).

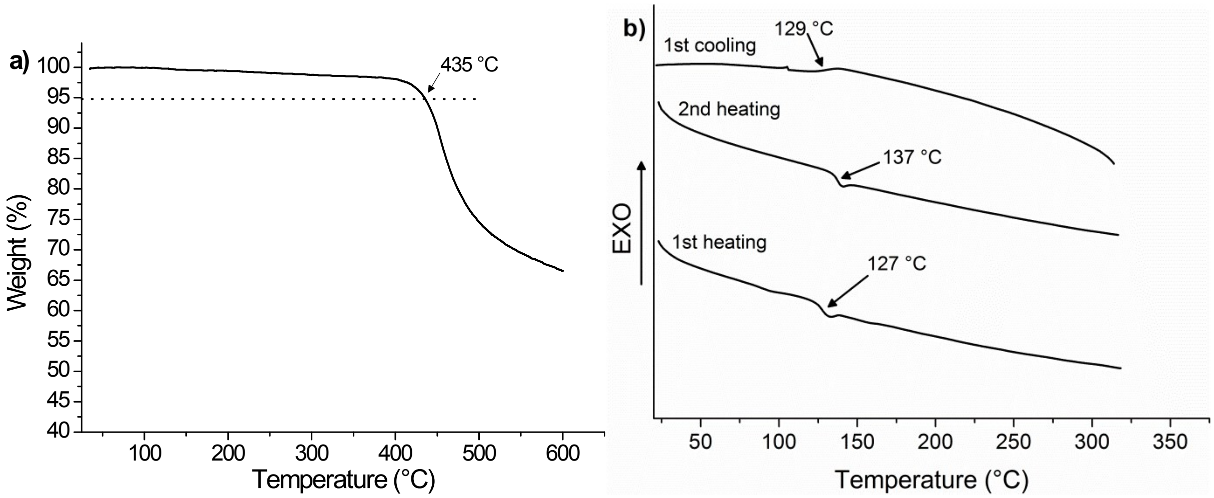
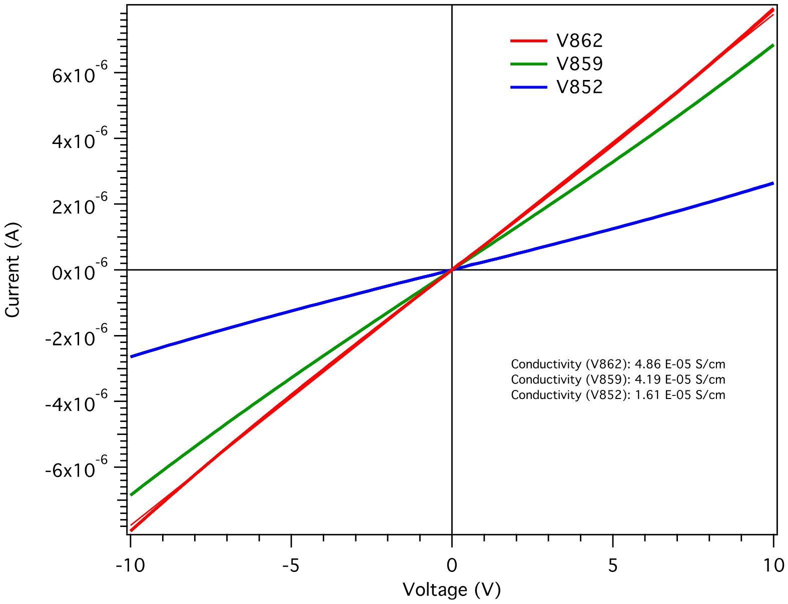


Figure S4. Thermogravimetric heating curve (a) and differential scanning calorimetry heating and cooling curves (b) of **V859** (heating/cooling rate 10 °K min^{-1}).



Conductivity (V862): 4.86 E-05 S/cm
Conductivity (V859): 4.19 E-05 S/cm
Conductivity (V852): 1.61 E-05 S/cm

Figure S5. Conductivity plot of doped thin films of HTM **V852**, **V859**, **V862**.

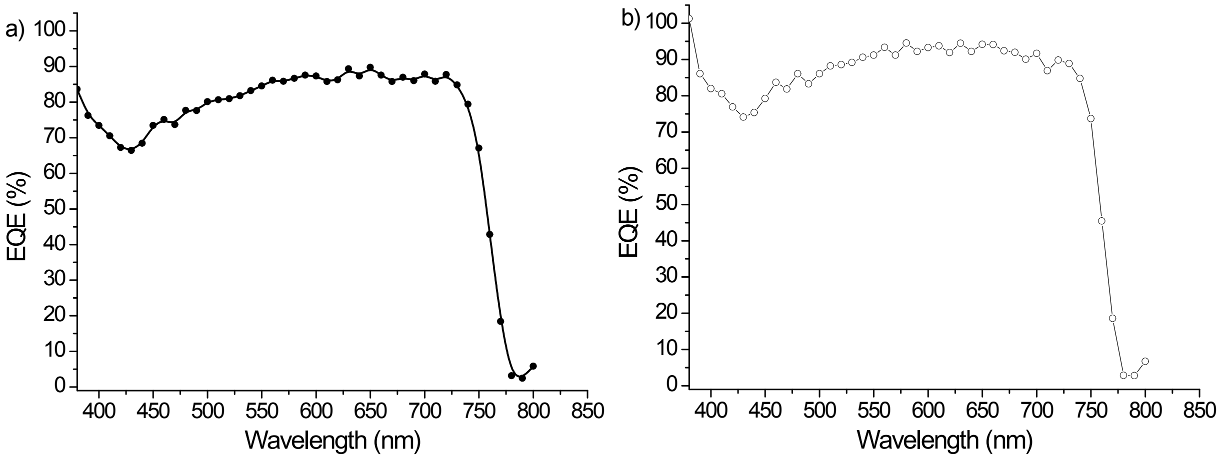


Figure S6. External quantum efficiency of a representative **V859** (a) and **V862** (b) devices with mixed perovskite.

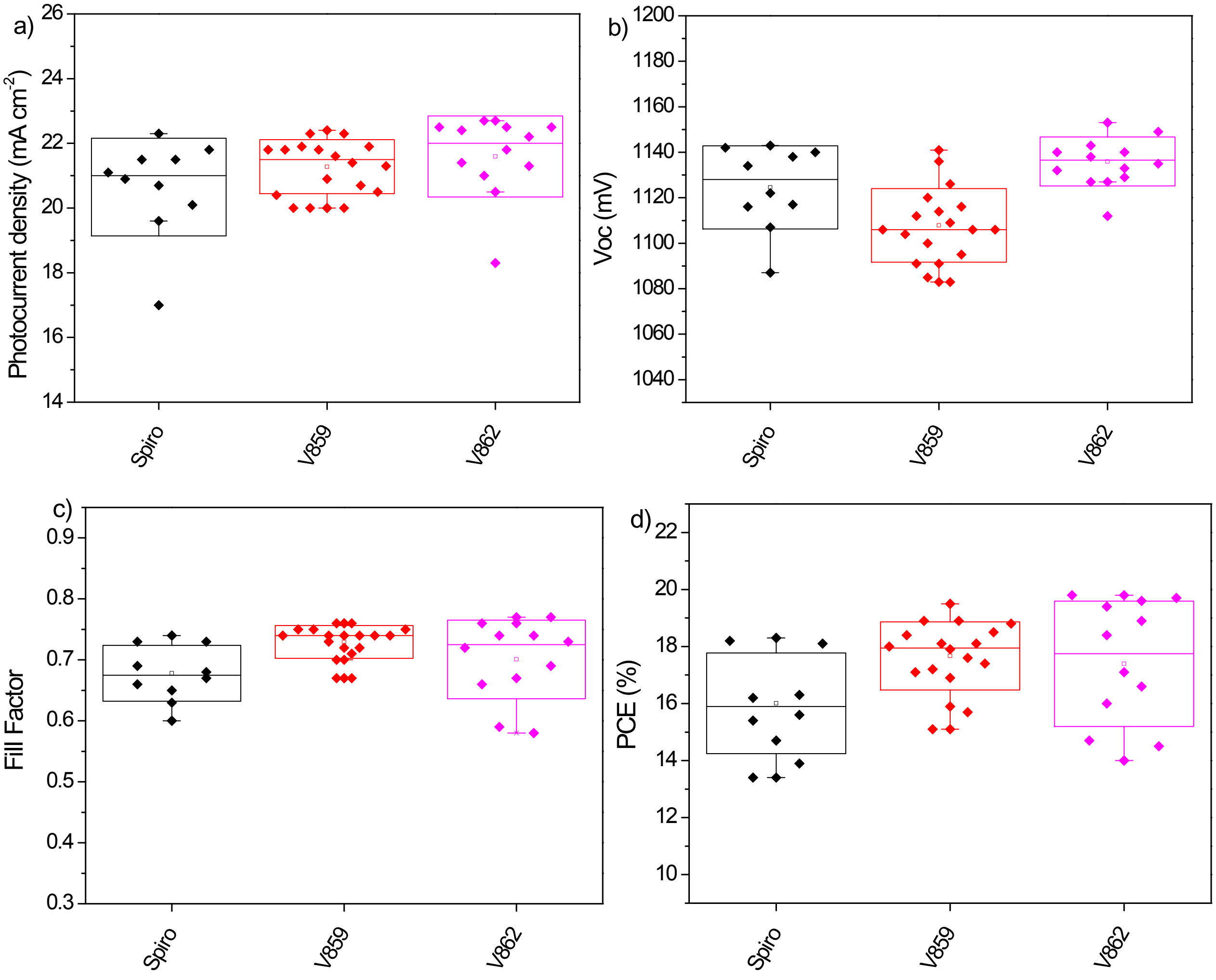


Figure S7. Device statistics of **V859**, **V862** and spiro-OMeTAD perovskite solar cells.

Table S5. Performance parameters of **V859** and **V862** devices measured after 50 days. Solar cells were stored under dry conditions.

HTM	**Time (h)**	**J_{sc} (mA cm^{-2})**	**V_{oc} (mV)**	**FF**	**PCE (%)**
V859	0	22.1	1099	0.67	16.34
	1200	22	1127	0.65	16.25
V862	0	20.5	1149	0.67	16.6
	1200	16.5	1125	0.56	10.2

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