## **Supporting Information**

# Synthesis of spiro[dibenzo[*c*,*h*]xanthene-7,9'-fluorene]-based dopant-free hole-transport materials for perovskite solar cells

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### **Experimental Section**

### **General Methodology**

Chemicals: 2,7-dibromo-9-fluorenone, 4-bromophenol, methane sulfonic acid, 4.4'dimethoxydiphenylamine, sodium tert-butoxide, tri-tert-butylphosphine, palladium(II) acetate, 1,1,2,2tetrachloroethane (TeCA), chlorobenzene (anhydrous 99.8%), acetonitrile (anhydrous 99.8%) and Spiro-OMeTAD were purchased from Sigma-Aldrich. PbI<sub>2</sub> (purity 98%) and PbBr<sub>2</sub> (purity 99.999%) were purchased from TCI and Alfa, respectively. Solvents and chemicals are commercially available and used as received unless specially stated. Chromatography was performed using silica gel 60 Å (35-63 µm). NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. High resolution MALDI spectra were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Varian 7.0TFTICR-MS). The UV-Visible absorption spectra were recorded on a Lambda 750 spectrophotometer. The steady-state photoluminescence (PL) spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. All the samples for UV-Visible and PL spectra were measured in a 1 cm cell at room temperature in dichloromethane (DCM). Time-resolved photoluminescence decay spectra were carried out with a LP920 laser flash spectrometer (Edinburgh Instruments). Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) were performed with a CH Instruments electrochemical workstation (model 660 A) using a conventional threeelectrode electrochemical cell. The SEM images were taken on a JEOL JSM-S4800. The light source for the photocurrent-voltage (J-V) measurements was an AM 1.5G solar simulator. The incident light intensity was 100 mW·cm<sup>-2</sup> calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.126 cm<sup>2</sup>. The photocurrent-voltage (*J-V*) curves were obtained by the linear sweep voltammetry (LSV) method using a Keithley 2400 source-measure unit with scan rate of 20 mV·s<sup>-1</sup>. The measurement of the incident-photon-to-current conversion efficiency (IPCE) was performed with a Xenon arc lamp (300 W), a 1/8 m monochromator, a source/meter and a power meter with an 818-UV detector head.

### **Device Fabrication**

Perovskite solar cells: The devices of PSCs were fabricated according to a published method.1 A 20~30 nm TiO<sub>2</sub> blocking layer was deposited on the cleaned FTO glass by spray pyrolysis using O<sub>2</sub> as the carrying gas at 450 °C from a precursor solution of 0.6 mL titanium diisopropoxide and 0.4 mL acetylacetonate in 7 mL anhydrous isopropanol. A 200 nm mesoporous TiO<sub>2</sub> was coated on the substrate by spin coating with a speed of 4500 rpm for 15 s with a ramp of 2000 rpm s<sup>-1</sup>, from a diluted 30 nm particle paste (Dyesol) in ethanol, the weight ratio of TiO<sub>2</sub> (Dyesol paste) and ethanol was 5.5:1. After that, the substrate was immediately dried on a hotplate at 80 °C, and then the substrates were sintered at 500 °C for 20 min. The perovskite film was deposited by spin coating onto the TiO<sub>2</sub> substrate with the following spin program: first at 2000 rpm for 10 s with a ramp of 200 rpm·s<sup>-1</sup>; second at 4000 rpm for 30 s with a ramp of 2000 rpm·s<sup>-1</sup>. During the spinning process, 110 µL chlorobenzene was dropped on the substrate during the second spin coating step 15 s before the end of the procedure. The perovskite precursor solution was prepared by mixing 461 mg PbI<sub>2</sub>, 43.75 mg FABr (formamidinium bromide), 11.2 mg MABr (methylamonium bromide), 77.4 mg FAI (formamidinium iodide), 13 mg CsI and 10.6 mg RbI in 750 µL mixed solvent of DMF (dimethylformamide) and DMSO (dimethyl sulfoxide) with a volume ratio of 4:1. The perovskite film was then sintered at 100 °C for 90 min on a hotplate. After cooling down to room temperature, HTM was subsequently deposited on the top of the perovskite layer by spin coating at 3000 rpm for 20 s. The HTM solution was prepared by dissolving the HTMs in chlorobenzene at a concentration of 18 mM, without additives. The HTM solution was dripped on the perovskite electrode and then followed by spin-coating for 30 s with 3000 rpm. All of the HTM solutions were prepared in a glove box under nitrogen atmosphere. Finally, 80 nm of gold was deposited by thermal evaporation using a shadow mask to pattern the electrodes.

### Synthesis of HTM X61 and X62



The compound 1 was synthesized according to reference.<sup>2</sup>

### Synthesis of 2',7'-dibromospiro[dibenzo[*c*,*h*]xanthene-7,9'-fluorene] (1).

A mixture of 2,7-dibromo-9-fluorenone (3.26 g, 9.64 mmol), 1-naphthol (5.56 g, 38.6 mmol) and methane sulfonic acid (MeSO<sub>3</sub>H, 2.5 mL, 3.7 g, 38.6 mmol) was heated at 150 °C under nitrogen for 24 h. The reaction mixture was then slowly added to deionized water and extracted with dichloromethane (DCM). The combined extracts were dried over MgSO<sub>4</sub>, evaporated and recrystallized with ethyl acetate to afford white solid (4.49 g, 79%).

<sup>1</sup>H NMR (400 MHz, DCM- $d_2$ )  $\delta$  8.79 (d, J = 8.4 Hz, 2H), 7.77 (td, J = 15.5, 7.9 Hz, 6H), 7.64 - 7.55 (m, 4H), 7.39 - 7.25 (m, 4H), 6.39 (d, J = 8.6 Hz, 2H).

#### Synthesis of 2',5,7',9-tetrabromospiro[dibenzo[c,h]xanthene-7,9'-fluorene] (2)

To a solution of **compound 1** (0.59 g, 1 mmol) in DCM (400 mL) under nitrogen  $Br_2$  (0.2 mL, 0.64 g, 4 mmol) was added. The resulting mixture was stirred at room temperature for 14 h. The solution was poured on 100 mL of water. 100 mL of DCM was added and it was washed with saturated  $Na_2S_2O_3$  (10 g). The organic layer was separated, dried over MgSO<sub>4</sub> and concentrated on a rotary evaporator to about 150 mL. The product was precipitated in MeOH (100 mL), filtrated and washed in MeOH (100 mL) to give yellow powder of crude product 0.65 g (87%). It was purified by crystallization in chloroform/ethanol mixture (1:1) to give 0.61 g (82%) of light yellow crystalline solid.

<sup>1</sup>H NMR (400 MHz, DCM- $d_2$ )  $\delta$  8.72 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H), 7.77 - 7.64 (m, 6H), 7.53 (d, J = 8.2 Hz, 2H), 7.21 (s, 2H), 6.56 (s, 2H).

# Synthesis of $N^{2'}, N^{7'}, N^{7'}$ -tetrakis(4-methoxyphenyl)spiro[dibenzo[c,h]xanthene-7,9'-fluorene]-2',7'-diamine (X61)

The synthesis of compound **X61** was achieved by Buchwald-Hartwig reaction in which 4,4'dimethoxydiphenylamine (1.0 g, 4.4 mmol), **compound 1** (1.18 g, 2 mmol), NaOtBu (0.42 g, 4.4 mmol), was added to 15 mL of dry toluene. The system was purged with nitrogen several times. Then  $P(t-Bu)_3$  (0.048 g, 0.24 mmol) and  $Pd(OAc)_2$  (0.054 g, 0.24 mmol) were combined in the mixture and the reaction was refluxed overnight. The organic phase was separated by ethyl acetate and the combined organic phases were dried with  $MgSO_4$  and purified by chromatography with petroleum ether/ethyl acetate (1:1) to afford 1.31 g (yield 74%) of **X61**.

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.60 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.75 - 7.60 (m, 6H), 7.53 (d, J = 8.7 Hz, 2H), 6.84 - 6.47 (m, 22H), 3.58 (s, 12H).

<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 155.77, 155.32, 147.68, 144.63, 139.94, 132.94, 132.06, 126.73,

125.90, 124.73, 123.42, 121.24, 120.21, 120.10, 118.24, 116.98, 114.60, 55.03.

HR-MS (ESI) m/z: calculated for 886.3407; found, 886.3388.

# Synthesis of $N^2', N^2', N^5, N^5, N^7', N^9, N^9$ -octakis(4-methoxyphenyl)spiro[dibenzo[c,h]xanthene-7,9'-fluorene]-2',5,7',9-tetraamine (X62)

The synthesis of compound X62 was achieved by Buchwald-Hartwig reaction in which 4,4'dimethoxydiphenylamine (0.75 g, 3.3 mmol), compound 2 (0.56 g, 0.75 mmol) and NaOtBu (0.32 g, 3.3 mmol) were added to 15 mL of dry toluene. The system was purged with nitrogen several times. Then P(t-Bu)<sub>3</sub> (0.036 g, 0.18 mmol) and Pd(OAc)<sub>2</sub> (0.040 g, 0.18 mmol) was placed in the mixture and the reaction was refluxed overnight. Organic phase separation was performed with ethyl acetate and the combined organic phases were dried with MgSO<sub>4</sub> and purified by chromatography with petroleum ether/ethyl acetate (1:1) to afford 0.849 g (yield 84%) of X62.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.66 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.74 - 7.66 (m, 2H), 7.58 - 7.48 (m, 4H), 6.80 - 6.52 (m, 36H), 6.26 (s, 2H), 3.64 (d, *J* = 13.2 Hz, 24H).

 $^{13}$ C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  155.27, 155.18, 154.00, 147.67, 142.87, 141.44, 140.16, 139.02,

132.05, 130.51, 127.36, 127.10, 125.41, 125.13, 125.03, 123.77, 121.98, 121.85, 121.39, 120.36,

118.53, 117.33, 114.57, 114.49, 55.15, 55.06.

HR-MS (ESI) m/z: calculated for 1340.5299; found, 1340.5304.

#### Characterization



Figure S1 <sup>1</sup>H NMR (DCM- $d_2$ ) spectrum of Compound 1.



Figure S2 <sup>1</sup>H NMR (DCM- $d_2$ ) spectrum of Compound 2.



Figure S3 <sup>1</sup>H NMR (DMSO- $d_6$ ) spectra of X61.



**Figure S4**  ${}^{13}$ C NMR (DMSO- $d_6$ ) spectra of **X61**.



**Figure S5** <sup>1</sup>H NMR (DMSO- $d_6$ ) spectra of **X62**.



Figure S7 Normalized UV-Visible absorption and photoluminescence of X61 and X62 in DCM ( $10^{-5}$  M).



Figure S8 Cyclic voltammetry (CV) spectra of X61, X62, Spiro-OMeTAD and ferrocene in DCM  $(10^{-4} \text{ M})$ .



Figure S9 Differential pulsed voltammetry (DPV) of X61 and X62.

HTMs	λ <sub>abs</sub>	[nm]	λ <sub>em</sub> [nm]	E <sub>0-0</sub> <sup>[a]</sup> [eV]	Eox <sup>[b]</sup> [V]	HOMO [c] [eV]	LUMO <sup>[d]</sup> [eV]
X61	310	379	432	3.02	0.64	-5.11	-2.09
X62	299	383	483	2.92	0.67	-5.14	-2.22
Spiro- OMeTAD	306	386	423	3.05	0.63	-5.10	-2.05

Table S1 Summary of optical and electrochemical properties of X61, X62 and Spiro-OMeTAD.

**[a]** Calculated from the intersection of the normalized absorption and emission spectrum. **[b]** 0.1 M of tetrabutylammoniun hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) in DCM as electrolyte; Ag/0.01 M AgNO<sub>3</sub> electrode (acetonitrile as solvent) as the reference electrode; a glassy carbon disk (diameter 3 mm) as the working electrode; a platinum wire as the counter electrode. Scan rate: 100 mV/s. All redox potentials were calibrated vs. normal hydrogen electrode (NHE) by the addition of ferrocene. The conversion  $E_{(Fc/Fc+)} = 630$  mV vs NHE was used.  $E_{1/2}^{Fc} = 0.20$  V. **[c]** HOMO = -5.1- ( $E_{1/2}-E_{1/2}^{Fc}$ ). **[d]** LUMO = HOMO +  $E_{0-0}$ .

### **Computational Details**

In the simulation, optimization and single point energy calculations are performed using the cam- $B3LYP^3$  and the 6-31G\*\* basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian  $09^4$ .



Figure S10 Frontier orbitals of X61 and X62.

## **Hole Mobility**

Hole mobility was investigated by the space charge limited current (SCLC) method, which can be described as the following equation:

$$J = \frac{9}{8}\mu\varepsilon_0\varepsilon_r\frac{V^2}{d^3}$$

where *J* is the current density,  $\mu$  is the hole mobility,  $\varepsilon_0$  is the vacuum permittivity (8.85 × 10<sup>-12</sup> F/m),  $\varepsilon_r$  is the dielectric constant of the material (normally taken to approach 3 for organic semiconductors), *V* is the applied bias, and d is the film thickness.

The hole-only devices were fabricated according to the literature.<sup>5</sup>

#### **Conductivity Measurements**

The electrical conductivities of the HTM films were determined by using a two-probe electrical conductivity measurements, which were performed by following a published procedure.<sup>6</sup> The obtained electrical conductivities are calculated by using the following equation:

$$\sigma = \frac{W}{RLD}$$

where *L* is the channel length 10 mm, *W* is the channel width 2 mm, *D* is the film thickness of the  $TiO_2$  and HTMs, and *R* is the film resistance calculated from the gradients of the curves.



Figure S11 Hole conductivity of X61, X62 and Spiro-OMeTAD films (without dopants).



Figure S12 Hole mobility of X61, X62 and Spiro-OMeTAD films (without dopants).



Table S2 Summary of hole mobility and conductivity of X61, X62 and Spiro-OMeTAD.





Figure S13 Top view of perovskite films without HTMs (a) and with different concentration of X61 (b) and X62 (c).



**Figure S14 (a)** Steady-state photoluminescence spectra at excitation wavelength of 530 nm and **(b)** time resolved fluorescence decay at 760 nm for the pristine perovskite film and the perovskite films capping different HTMs.

## Crystallography

The diffraction data of X61 and X62 were measured at 298 K and 100K respectively by using Cu K $\alpha$  radiation on a Bruker D8 VENTURE single crystal X-ray diffractometer equipped with a kappa geometry goniometer. The dataset was reduced and absorption correction was applied in APEX3 suite. The crystal structure was solved and refined by SHELXT and SHELXL respectively.<sup>7</sup> The crystal structure was refined using full-matrix least-squares based on F<sup>2</sup> with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table S3.



**Figure S15** Molecular conformations of **X61** (a, b, c) and **X62** (d, e, f) obtained from SCXRD. The grey, red, and blue colored atoms represent C, O, and N, respectively. Hydrogen atoms are omitted for clarity.



Figure S16 Perspective views of X61 (a, b, c) and X62 (d, e, f) molecules in one unit cell along different axis obtained from SCXRD.



Figure S17 Crystal packing of X61 (a, b, c) and X62 (d, e, f) molecules along crystallographic axes.

	X61	X62
Empirical formula	$C_{61}H_{46}N_2O_5$	C <sub>89</sub> H <sub>72</sub> N <sub>4</sub> O <sub>9</sub>
Formula weight	887.05	1341.57
Crystal color, habit	Light orange, block	Yellow, needle
Crystal system	triclinic	monoclinic
a, Å	10.6341(5)	21.310(4)
b, Å	16.3753(7)	22.284(5)
c, Å	17.6369(8)	16.397(3)
α, deg	64.812(2)	90
β, deg	87.802(2)	95.97(3)
γ, deg	88.570(2)	90
V, Å <sup>3</sup>	2777.0(2)	7744(3)





Figure S18 X-ray diffraction (XRD) pattern of the mixed perovskite film.



Figure S19 *J-V* curves from different scan directions for the devices based on Spiro-OMeTAD (a), X61 (b) and X62 (c).



**Figure S20** Stability of the unsealed PSCs based on the different dopant-free HTMs **Spiro-OMeTAD**, **X61** and **X62** recorded at high humidity (50%) under 100 mW cm<sup>-2</sup> AM1.5G for around 10 days.



Figure S21 Electrochemical impedance spectroscopy (EIS) results for PSCs based on Spiro-OMeTAD, X61 and X62.

Table S4 Summary of resistances from EIS of X61, X62 and Spiro-OMeTAD.

HTMs	$\mathbf{R}_{\mathrm{s}}\left[\Omega ight]$	$\mathbf{R}_{\mathrm{rec}}\left[\Omega ight]$
X61	11.4	651.7
X62	8.2	1567.3
Spiro-OMeTAD	9.7	713.3

References

- D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa-Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Sci. Adv.*, 2016, 2, 1501170.
- 2. F. Liu, L.-H. Xie, C. Tang, J. Liang, Q.-Q. Chen, B. Peng, W. Wei, Y. Cao and W. Huang, *Org. Lett.*, 2009, **11**, 17.
- 3. A. D. Becke, J. Chem. Phys., 1993, 98, 1372.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009).
- 5. B. Xu, D. Bi, Y. Hua, P. Liu, M. Cheng, M. Grätzel, L. Kloo, A. Hagfeldt and L. Sun, *Energy Environ. Sci.*, 2016, 9, 873-877.
- 6. H. J. Snaith and M. Grätzel, Appl. Phys. Lett., 2016, 89, 262114.
- 7. G. M. Sheldrick, Acta Crystallogr. Sect. A: Found. Crystallogr., 2007, 64, 112-122.
- 8. V. Gonzalez-Pedro, E. J. Juarez-Perez, W. S. Arsyad, E. M. Barea, F. Fabregat-Santiago, I. Mora-Sero and J. Bisquert, Nano Lett., 2014, 14, 888-893.