

# Supplementary Information

## Novel Carbazole-Based Hole-Transporting Materials with Star-Shaped Chemical Structures for Perovskite-Sensitized Solar Cells

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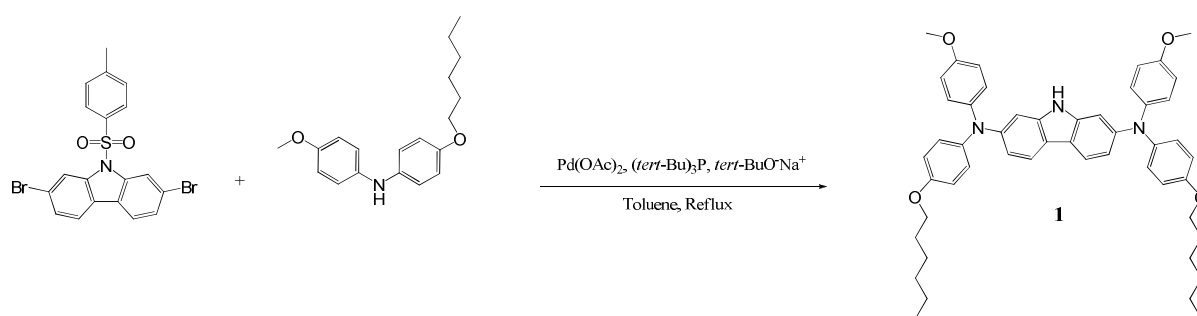
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## General

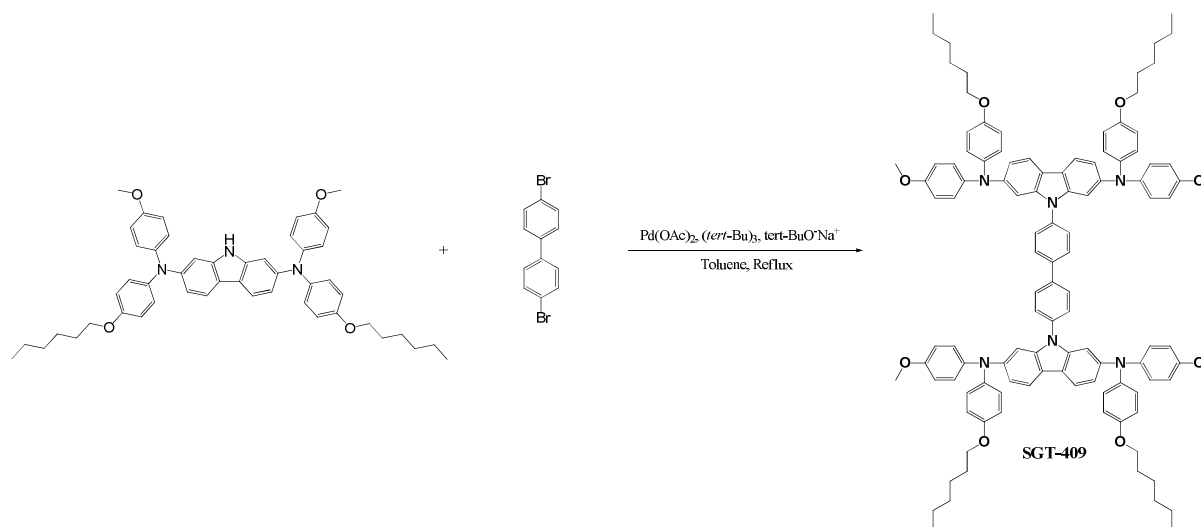
1,3,5-Tribromobenzene, 1,4-dibromobenzene and 4,4'-dibromobiphenyl were purchased from Sigma–Aldrich. 1,3,5-Tris(4-bromophenyl)benzene was purchased from Tokyo Chemical Industry Co., Ltd. 2,7-Dibromo-9-tosyl-9H-carbazole,<sup>1,2</sup> was prepared by slight modification of a previously reported procedure. The intermediate material N2,N7-bis(4-(hexyloxy)phenyl)-N2,N7-bis(4-methoxyphenyl)-9H-carbazole-2,7-diamine and new hole-transport materials (HTMs) were synthesised through conventional palladium-catalysed Buchwald–Hartwig amination by using Pd(OAc)<sub>2</sub>, (*tert*-Bu)<sub>3</sub>P and *tert*-BuO<sup>−</sup>Na<sup>+</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy studies were conducted with a Varian Mercury 300 spectrometer, using tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 spectrometer, using tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. MALDI-TOF mass spectra were recorded on a Voyager-DE STR biospectrometry workstation. GC–mass spectra were recorded on a JEOL JMS-600W mass spectrometer. FT-IR spectra were acquired by using a Jasco FT/IR-4200 spectrometer with a KBr pellet. Thermal analysis was conducted using sino DSC N-650 and TGA N-1000 equipment. All DSC data were collected from the second cycle of the DSC curve.

## Synthesis



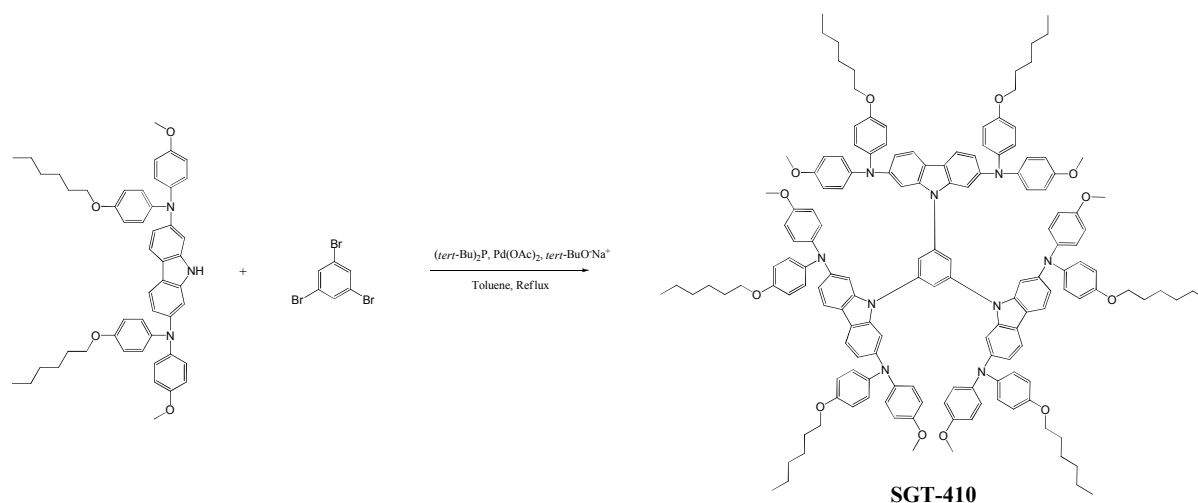
**1:** 2,7-Dibromo-9-tosyl-9H-carbazole (4.24 g, 8.85 mmol), N2,N7-bis(4-(hexyloxy)phenyl)-N2,N7-bis(4-methoxyphenyl)-9H-carbazole-2,7-diamine (5.43 g, 18.14 mmol), palladium acetate (0.4 g, 1.77 mmol), tri-*tert*-butylphosphine (0.72 g, 3.54 mmol) and sodium *tert*-butoxide (10.2 g, 106.18 mmol) dissolved in 20 mL of anhydrous toluene were refluxed for 5 days under a nitrogen atmosphere prior to being quenched with distilled water.

The mixture was extracted with ethyl acetate and washed several times with brine. The organic layer was dried with anhydrous magnesium sulfate. The filtrate was then evaporated under a vacuum and purified through column chromatography (EA : Hex = 1 : 5) to give **1** (5.5 g, 82 %) as a brown solid.  $^1\text{H}$  NMR (300 MHz; DMSO- $d^6$ ; TMS)  $\delta$  (ppm) 10.60 (1 H, s, Ar-NH), 7.73 (2 H, d,  $J=8.4$  Hz, Ar-H), 6.98 (8 H, m, Ar-H), 6.82 (8 H, m, Ar-H), 6.75 (2 H, s, Ar-H), 6.65 (2 H, d,  $J=8.4$  Hz, Ar-H), 3.92 (4 H, t,  $J=6.9$  Hz, Ar-OCH<sub>2</sub>-), 3.73 (6H, s, Ar-OCH<sub>3</sub>), 1.69 (4H, m, -CH<sub>2</sub>-), 1.48 (12H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.88 (12H, m, -CH<sub>3</sub>). FT-IR (KBr) [ $\text{cm}^{-1}$ ] 3400 (-NH).

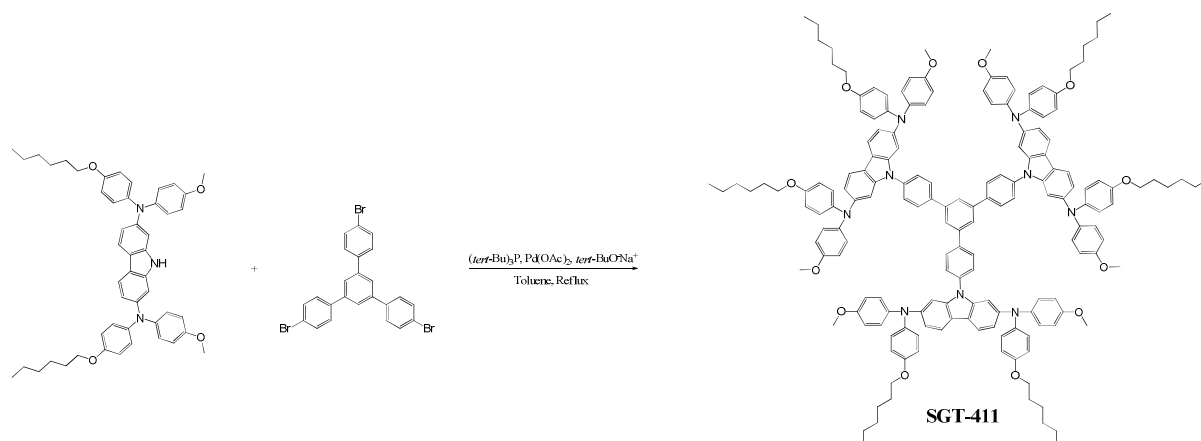


**SGT-409: 1** (1.05 g, 1.38 mmol), 4,4'-dibromobiphenyl (0.21 g, 0.67 mmol), palladium acetate (0.03 g, 0.13 mmol), tri-*tert*-butylphosphine (0.05 g, 0.27 mmol) and sodium *tert*-butoxide (0.78 g, 8.08 mmol) dissolved in 20 mL of toluene were refluxed for 5 days under a nitrogen atmosphere prior to being quenched with distilled water. The mixture was extracted with ethyl acetate and washed several times with brine. The organic layer was dried with anhydrous magnesium sulfate. The filtrate was then evaporated under a vacuum and purified through column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-409** (0.52 g, 46 %) as a brown solid.  $^1\text{H}$  NMR (300 MHz; THF- $d^8$ ; TMS)  $\delta$  (ppm) 7.81 (4 H, d,  $J=8.1$  Hz, Ar-H), 7.61 (4 H, d,  $J=8.1$  Hz, Ar-H), 7.43 (4 H, d,  $J=8.4$  Hz, Ar-H), 7.05 (4 H, s, Ar-H), 6.96 (16 H, d,  $J=7.2$  Hz, Ar-H), 6.84 (4 H, d,  $J=8.4$  Hz, Ar-H), 6.75 (4 H, d,  $J=8.4$  Hz, Ar-H), 3.89 (8 H, t, Ar-OCH<sub>2</sub>-), 3.69 (12 H, s, Ar-OCH<sub>3</sub>), 1.46 (8 H, m, -CH<sub>2</sub>-), 1.33 (24 H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), (12 H, m, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz; THF- $d^8$ ; TMS)  $\delta$  (ppm) 156.32, 155.86, 147.56, 142.78, 142.60, 142.46, 139.35, 137.71, 128.82, 127.14, 126.06, 125.96,

120.39, 119.42, 117.37, 115.63, 115.05, 104.35, 68.52, 55.35, 32.40, 30.14, 26.54, 23.34, 14.21. HRMS-MS (MALDI-TOF):  $m/z$  found: 1673.9, calcd.: 1674.15.



**SGT-410:** **1** (2.21 g, 2.91 mmol), 1,3,5-tribromobenzene (0.3 g, 0.95 mmol), palladium acetate (0.06 g, 0.29 mmol), tri-*tert*-butylphosphine (0.12 g, 0.57 mmol) and sodium *tert*-butoxide (1.37 g, 14.29 mmol) dissolved in 20 mL of toluene were refluxed for 5 days under a nitrogen atmosphere prior to being quenched with distilled water. The mixture was extracted with ethyl acetate and washed several times with brine. The organic layer was dried with anhydrous magnesium sulfate. The filtrate was then evaporated under a vacuum and purified through column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-410** (1.24 g, 55%) as a brown solid.  $^1\text{H}$  NMR (300 MHz; THF- $d^8$ ; TMS)  $\delta$  (ppm) 7.84 (6 H, d,  $J=8.7$  Hz, Ar-H), 7.44 (3 H, s, Ar-H), 7.09 (6 H, s, Ar-H), 6.86 (30 H, m, Ar-H), 6.53 (12 H, d,  $J=9.3$  Hz, Ar-H), 6.40 (12 H, d,  $J=8.7$  Hz, Ar-H), 3.71 (12 H, t, Ar-OCH<sub>2</sub>-), 3.45 (18 H, s, Ar-OCH<sub>3</sub>), 1.41 (48 H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.92 (18H, t, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz; THF- $d^6$ ; TMS)  $\delta$  (ppm) 157.43, 157.06, 148.38, 143.02, 142.93, 141.94, 141.62, 127.35, 127.15, 121.77, 120.56, 118.30, 117.37, 116.49, 115.85, 104.35, 69.45, 56.42, 56.39, 33.51, 31.21, 27.61, 24.42, 15.28. HRMS-MS (MALDI-TOF):  $m/z$  found: 2357.7, calcd.: 2358.03.



**SGT-411:** **1** (0.77 g, 1.01 mmol), 1,3,5-tris(4-bromophenyl)benzene (0.18 g, 0.33 mmol), palladium acetate (0.02 g, 0.10 mmol), tri-*tert*-butylphosphine (0.04 g, 0.20 mmol) and sodium *tert*-butoxide (0.48 g, 4.97 mmol) dissolved in 20 mL of toluene were refluxed for 5 days under a nitrogen atmosphere prior to being quenched with distilled water. The mixture was extracted with ethyl acetate and washed several times with brine. The organic layer was dried with anhydrous magnesium sulfate. The filtrate was then evaporated under a vacuum and purified through column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-411** (0.4 g, 47%) as a brown solid.  $^1\text{H}$  NMR (300 MHz; THF- $d^8$ ; TMS)  $\delta$  (ppm) 7.83 (12 H, m, Ar-H), 7.50 (6 H, d,  $J=8.7$ , Ar-H), 7.06 (6 H, s, Ar-H), 6.97 (24 H, m, Ar-H), 6.84 (9 H, m, Ar-H), 6.76 (24 H, m, Ar-H), 3.88 (12 H, t, Ar-OCH<sub>2</sub>-), 3.68 (18H, s, Ar-OCH<sub>3</sub>), 1.29 (48H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.86 (18H, m, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz; THF- $d^6$ ; TMS)  $\delta$  (ppm) 157.31, 156.94, 148.58, 143.94, 143.62, 143.44, 141.33, 138.86, 130.27, 128.56, 127.17, 126.77, 121.55, 120.41, 118.52, 118.15, 116.85, 116.50, 116.29, 115.94, 110.00, 69.53, 56.36, 33.44, 31.16, 27.58, 24.39, 14.97. HRMS-MS (MALDI-TOF):  $m/z$  found: 2585.4, calcd.: 2586.32.

## References

- (a) A. W. Freeman, M. Urvoy, M. E. Criswell, *J. Org. Chem.*, **2005**, *70*, 5014; (b) D. Patra, D. Sahu, H. Padhy, D. Kekuda, C.-H. Chu, H.-C. Lin, *J. Polymer Sci.: Part A*, **2010**, *48*, 5479.
- B. Urones, R. G. Arrayás, J. C. Carretero, *Org. Lett.*, **2013**, *15*, 1120.

## Device Fabrication

An approximately 10 nm-thick Ti film was deposited on patterned fluorine-doped tin oxide (FTO)-coated glass (Pilkington, TEC8) as a TiO<sub>2</sub> compact layer, using an RF magnetron sputtering system (A-Tech system, Korea) followed by oxidation at 500°C for 30 min in air. A porous TiO<sub>2</sub> layer with a thickness of approximately 200 nm was then spin-coated at 5000 rpm for 30 s, using a paste derived from 50 nm-sized TiO<sub>2</sub> nanoparticles. The coated film was then heated at 500°C for 30 min. A CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer was deposited by using a two-step method that was reported previously.<sup>S1</sup> A PbI<sub>2</sub> solution in *N,N*-dimethylformamide (462 mg mL<sup>-1</sup>), which was kept at 70°C, was coated onto the porous TiO<sub>2</sub> films by spin coating at 6000 rpm for 60 s. It was dried at 70°C for 30 min and then cooled to room temperature. The film was then immersed in a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> 2-propanol solution (10 mg mL<sup>-1</sup>) for 20 s, and washed with 2-propanol, followed by drying at 70°C for 15 min. For the **HTM** layers, **SGT-409**, **SGT-410**, **SGT-411** and *spiro-MeOTAD* [2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene] were coated onto substrates by spin-coating at 5000 rpm for 30 s. The composition of the **HTMs**, used for spin coating, were 79 mg for **SGT-409**, 55.64 mg for **SGT-410**, 61.03 mg for **SGT-411** and 72.3 mg for *spiro-MeOTAD* in 1 mL of chlorobenzene, 28.8 µL of 4-*tert*-butylpyridine, 17.5 µL of lithium bis(trifluoromethylsulfonyl) imide in 1 mL of acetonitrile and 29 µL of tris(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine) cobalt(III) bis(trifluoromethylsulfonyl) imide in 1 mL acetonitrile. An Au layer with a thickness of 60 nm was deposited by thermal evaporation (Korea Vacuum Tech.) to form the back contact. The active area of the device was defined by a metal mask with a size of 0.30 cm<sup>2</sup>.

## Device Characterization

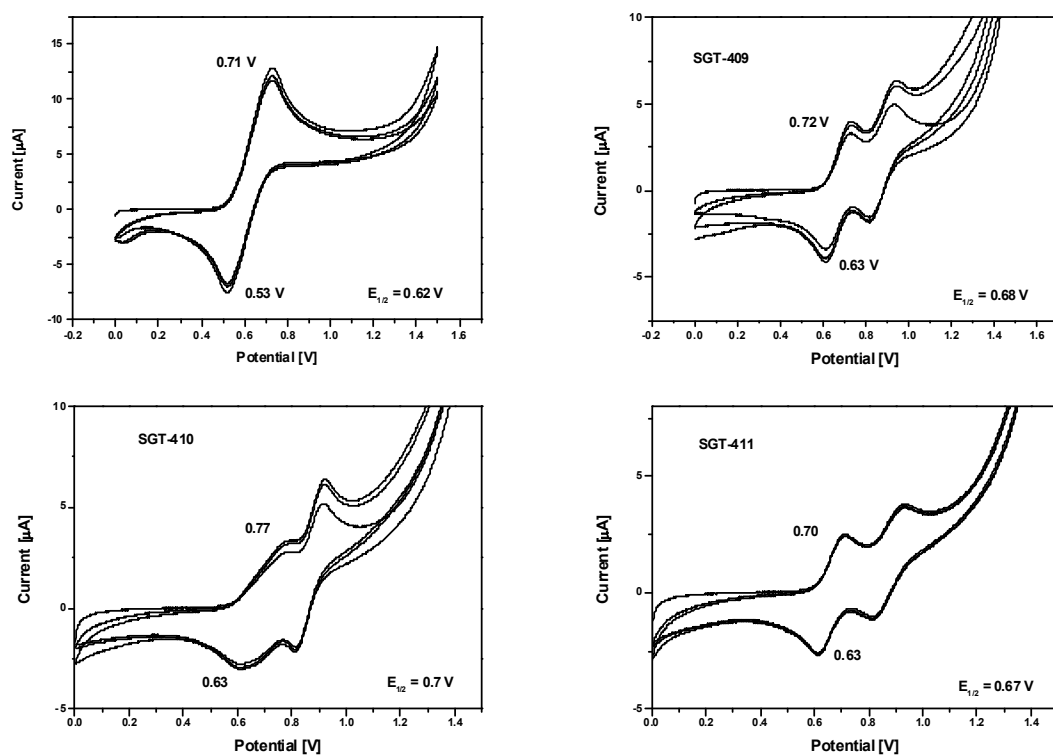
The morphologies of the prepared TiO<sub>2</sub> films were examined by field-emission scanning electron microscopy (FESEM, Hitachi S4300). Photocurrent–voltage (*I*–*V*) measurements were performed by using a Keithley model 2400 source measurement unit. A 300 W Xenon lamp (Spectra-Physics) was used as the light source and the light intensity was adjusted by using an NREL-calibrated Si solar cell equipped with a KG-5 filter for approximating AM 1.5 G one-sunlight intensity. The magnitude of the alternate signal was 10 mV. The impedance parameters were determined by fitting the impedance spectra using Z-view software. The incident photon-to-current efficiency (IPCE) spectra were measured as a

function of wavelength from 400 to 900 nm using a specially designed IPCE system (PV Measurements, Inc.). UV/Vis absorption spectra of the **HTMs** in solution were measured with a Shimadzu UV-2401PC spectrophotometer.

For the electrochemical measurements, cyclic voltammetry (CV) was carried out with *VersaSTAT3* (AMETEK) equipment, using a typical three-electrode electrochemical cell in a solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte in water-free THF at a scan rate of 50 mV s<sup>-1</sup> at room temperature; the sample was degassed with argon gas for 10 min prior to the scan. Potentials were calibrated in reference to the Fc<sup>+</sup>/Fc couple.

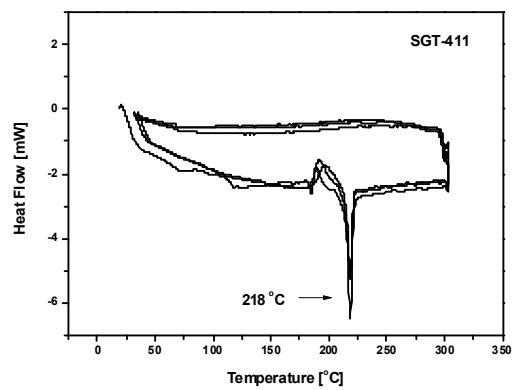
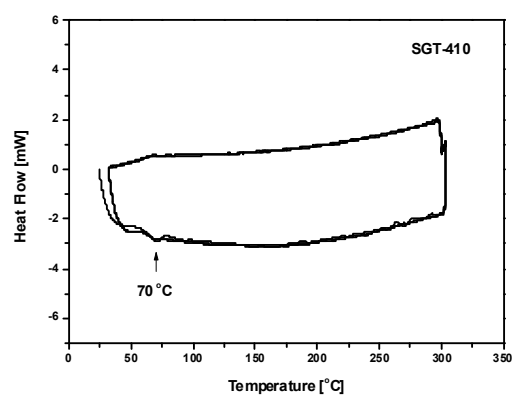
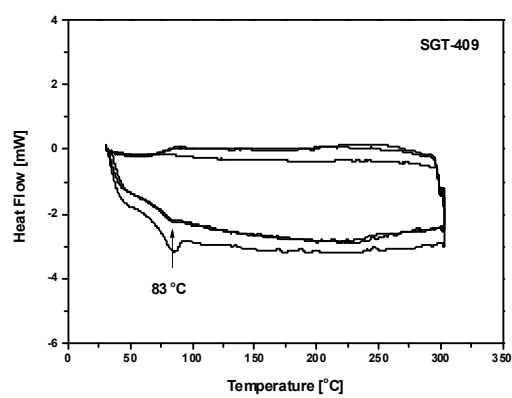
For the conductivity measurements, substrates that were used for two-probe electrical conductivity measurements consisted of boron-silicate glass substrate, on which 40 nm Au electrodes were deposited with a shadow mask, patterned to yield a channel length and width of 100 μm and 500 μm, respectively. As a cleaning step, the substrates were sonicated in acetone and methanol, and subsequently rinsed with DI water. The hole conductor was then deposited by spin-coating a 5 wt% solution of **HTMs** in toluene. The *I-V* characteristics were recorded on an Agilent B1500 Semiconductor analyser. The film thickness was measured using an R2 alpha-step surface profilometer (TENCOR Instrument). Conductivity values for the **HTMs**, including *spiro-OMeTAD*, were collected at a 20 V applied bias.

Time-resolved photoluminescence (TR-PL) was measured by using a time-correlated single-photon counting (TCSPC) spectrometer (FluoTime 200, PicoQuant). Film samples of **HTM**/perovskite deposited on pyrex glass substances were excited by 100 ps, 393 nm laser pulses, which were incident on the **HTM** side (that is, front illumination), and the emission from the sample was collected at the wavelength of 760 nm. The nominal temporal resolution of the TR-PL measurement was approximately 190 ps, but the practical time resolution was tens of picoseconds after deconvolution of the instrument response function.

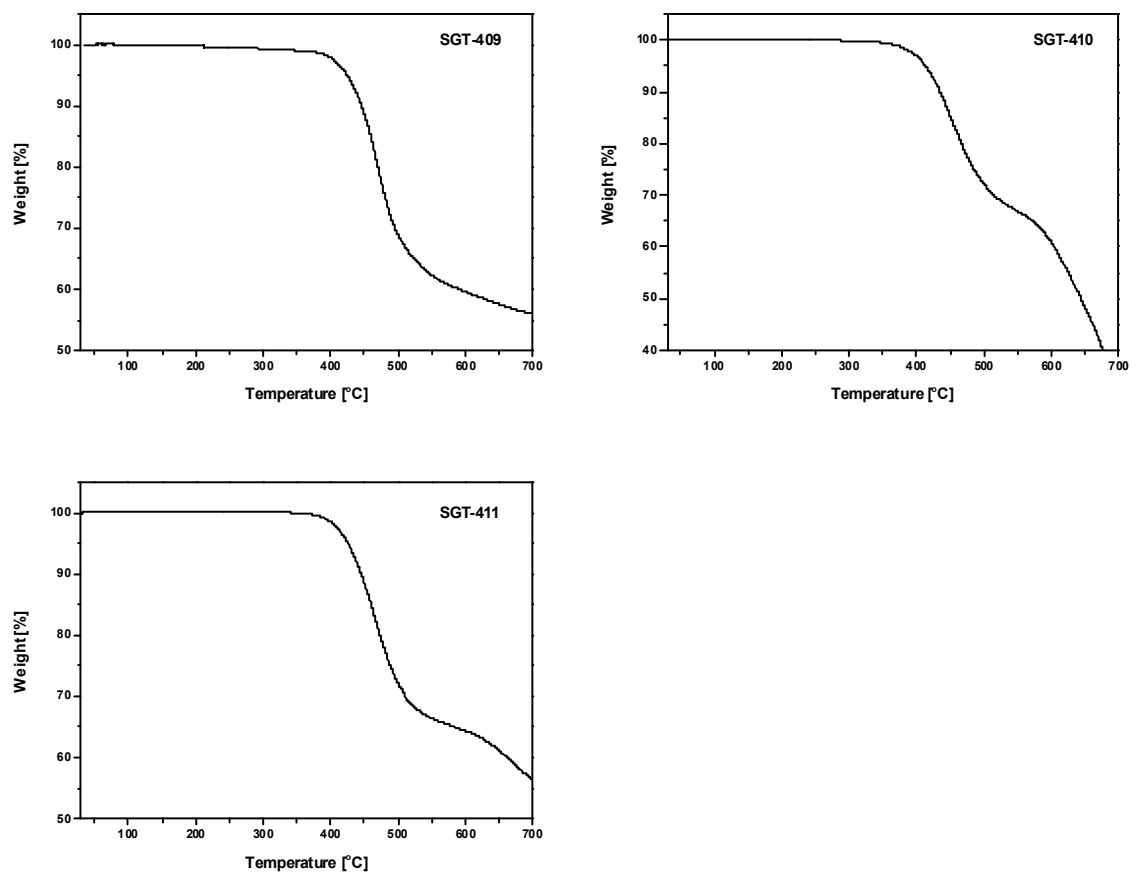


**Fig. S1** Cyclic voltammograms of the new **HTMs** and the FC/FC<sup>+</sup> redox couple in THF with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte with a scan rate of 50 mV s<sup>-1</sup>.

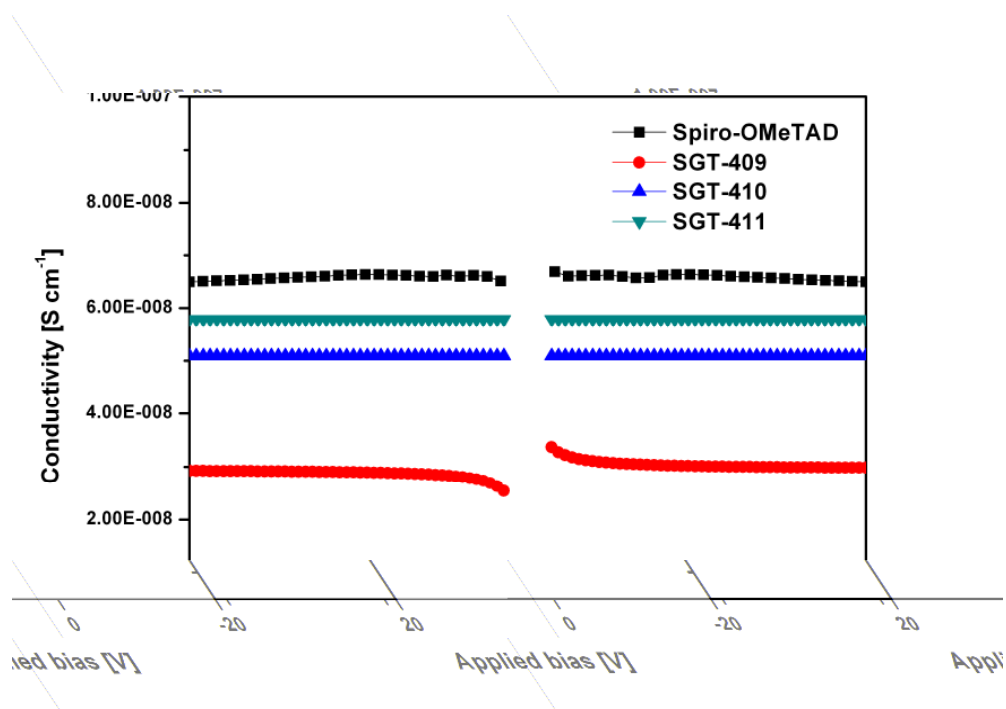




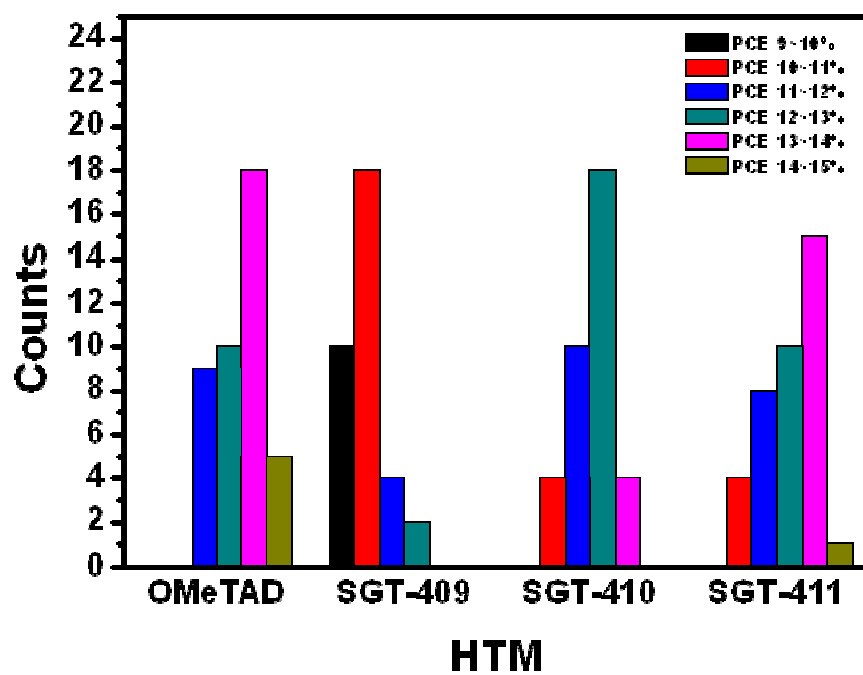
**Fig. S2** Differential scanning calorimetry of new **HTMs** with a scan rate of  $20^{\circ}\text{C min}^{-1}$ .



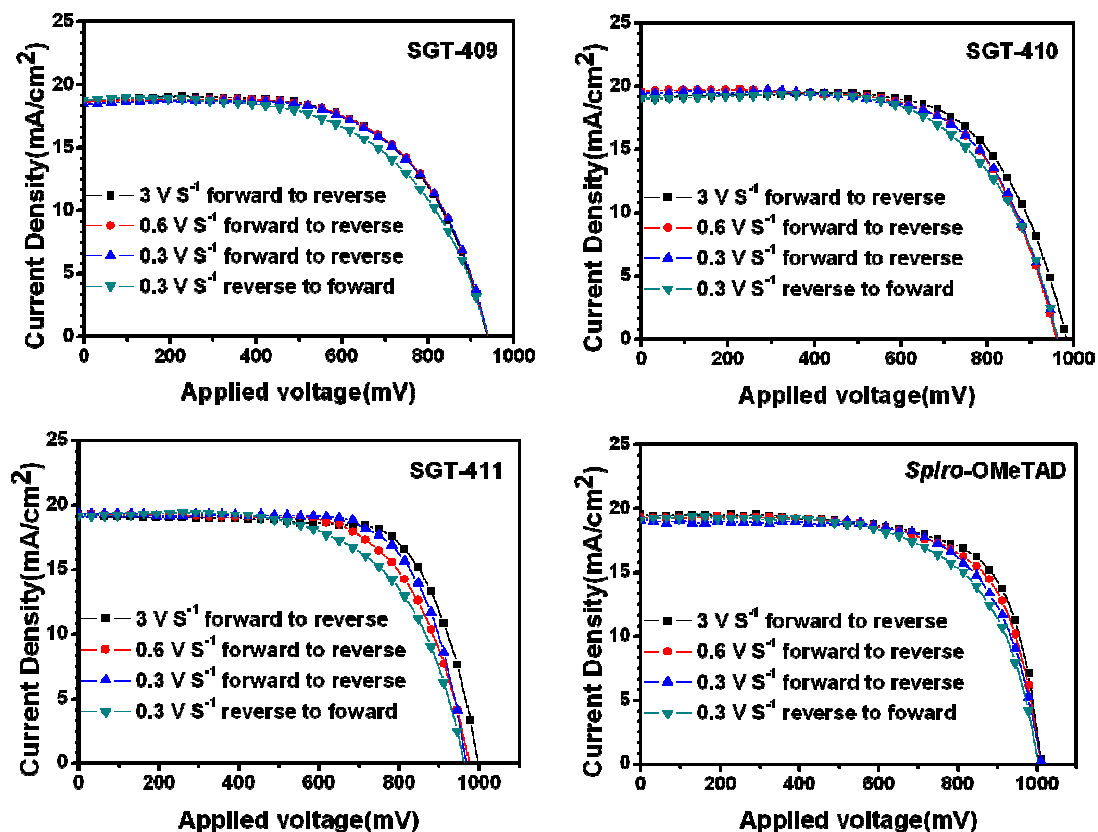
**Fig. S3** Thermogravimetric analysis of the new **HTMs** with a scan rate of 15 °C min<sup>-1</sup>.



**Fig. S4** Conductivity of the new **HTMs** derived from  $I$ - $V$  curve by using  $\sigma = L/Rwt$ , where  $L$  is the channel length,  $w$  is the channel width,  $t$  is the film thickness and  $R$  is the film resistance calculated from the gradients of the curves.



**Fig. S5** Histogram of solar cell efficiencies for 30 times of different HTMs.



**Fig. S6** Perovskite solar cells employing various HTMs measured by forward and reverse scans with 30mV voltage step and 100 ms delay time for  $J$ - $V$  data.

**Table S1.** The photovoltaic performance data of perovskite solar cells employing new HTMs

HTM	Scan conditions	Voc (V)	Jsc (mA/cm <sup>2</sup> )	Fill Factor (%)	Efficiency (%)
SGT-409	3 V S <sup>-1</sup> forward to reverse	0.938	18.653	62.65	10.96
	0.6 V S <sup>-1</sup> forward to reverse	0.938	18.634	62.70	10.96
	0.3 V S <sup>-1</sup> forward to reverse	0.939	18.479	62.62	10.87
	0.3 V S <sup>-1</sup> reverse to forward	0.939	18.770	58.10	10.25
SGT-410	3 V S <sup>-1</sup> forward to reverse	0.984	19.090	67.20	12.61
	0.6 V S <sup>-1</sup> forward to reverse	0.960	19.600	64.82	12.20
	0.3 V S <sup>-1</sup> forward to reverse	0.963	19.490	64.95	12.19
	0.3 V S <sup>-1</sup> reverse to forward	0.961	19.000	63.47	11.60
SGT-411	3 V S <sup>-1</sup> forward to reverse	0.997	19.315	67.49	13.00
	0.6 V S <sup>-1</sup> forward to reverse	0.975	19.308	67.01	12.62
	0.3 V S <sup>-1</sup> forward to reverse	0.968	19.320	66.03	12.35
	0.3 V S <sup>-1</sup> reverse to forward	0.962	19.127	62.50	11.50
Spiro-OMeTAD	3 V S <sup>-1</sup> forward to reverse	1.011	19.586	69.48	13.76
	0.6 V S <sup>-1</sup> forward to reverse	1.010	19.307	67.78	13.21
	0.3 V S <sup>-1</sup> forward to reverse	1.011	19.125	67.52	13.05
	0.3 V S <sup>-1</sup> reverse to forward	1.003	19.114	64.06	12.28
<b>Reference</b>					

S1. J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature*, **2013**, *499*, 316–319.