

Supplementary Information

14.8% Perovskite Solar Cells Based on Carbazole Derivatives as Hole Transporting Materials

*Sang Do Sung,^{‡a} Min Soo Kang,^{‡ b} In Taek Choi,^{‡b} Hong Mo Kim,^b Hyoungjin Kim,^c
MunPyo Hong,^c Hwan Kyu Kim^{*b} and Wan In Lee^{*a}*

*^a Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751,
Korea. E-mail: wanin@inha.ac.kr*

*^b Global GET-Future Lab. & Department of Advanced Materials Chemistry, Korea
University, Sejong 339-700, Korea. . E-mail: hkk777@korea.ac.kr*

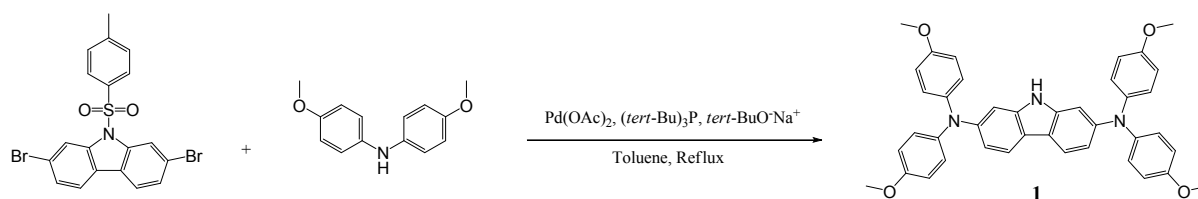
*^c Department of Display & Semiconductor Physics, Korea University, Sejong 339-700,
Korea.*

[‡]These authors contributed equally to this work.

General

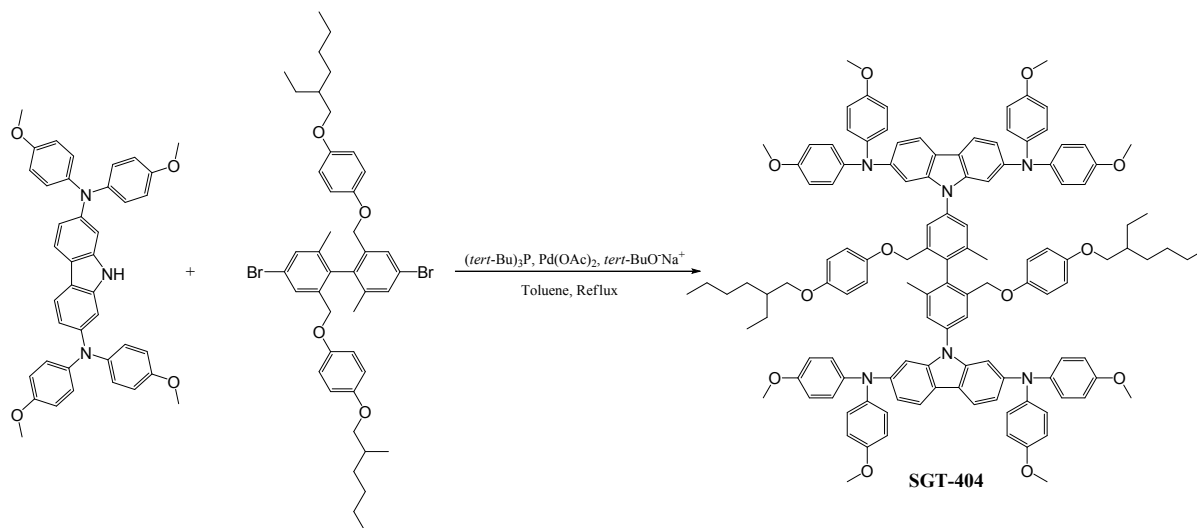
1,3,5-tribromobenzene, triphenylamine were purchased from sigma-aldrich. Tris(4-bromophenyl)amine,¹⁻² 2,7-dibromo-9-tosyl-9H-carbazole,³⁻⁴ 4,4'-dibromo-2,2'-bis((4-(2-ethylhexyloxy)-phen-oxy)methyl)-6,6'-dimethylbipheny⁵ were prepared by the slight modification of literature procedure. Intermediate material 2,7-bis(bis(4-methoxyphenyl)methyl)-9H-carbazole and new HTMs were synthesized through conventional palladium-catalyzed Buchwald-Hartwig amination using Pd(OAc)₂, (*tert*-Bu)₃P and *tert*-BuO⁻Na⁺. The ¹H & ¹³C NMR spectroscopy studies were conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. Chemical shifts for ¹H & ¹³C 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 by a Voyager-DE™ STR biospectrometry workstation. GC mass spectra were recorded by a JEOL JMS-600W mass spectroscopy. FT-IR spectra were acquired using a Jasco FT/IR-4200 spectrometer with a KBr pellet. Thermal analysis was conducted using sinco DSC N-650 and TGA N-1000. All DSC data were collected from second cycle of DSC curve.

Synthesis

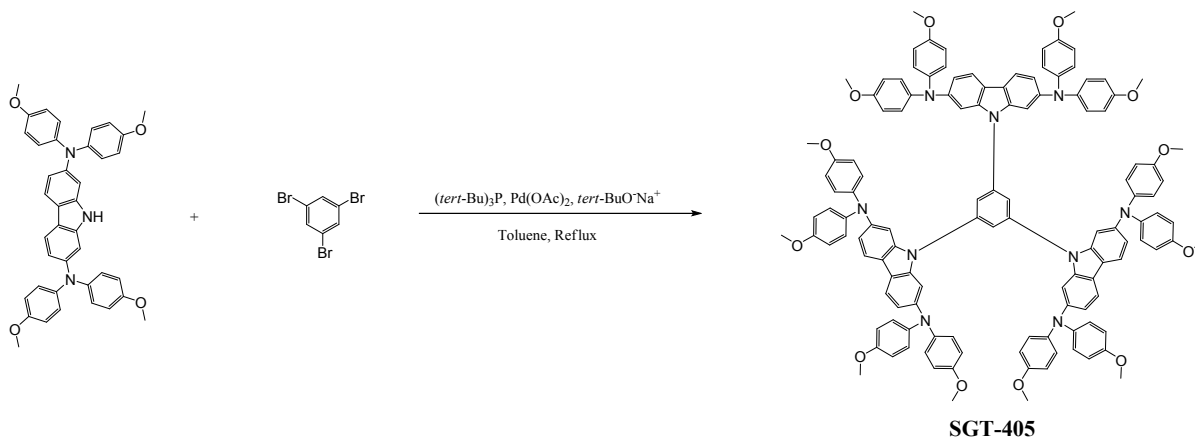


1: 2,7-dibromo-9-tosyl-9H-carbazole (1 g, 2.09 mmol), bis(4-methoxyphenyl)amine (1 g, 4.38 mmol), Palladium acetate (0.02 g, 0.1 mmol), tri-*tert*-butylphosphine (0.08 g, 0.42 mmol) and sodium *tert*-butoxide (0.6 g, 6.26 mmol) dissolved in 20 ml of anhydrous toluene were refluxed 5 days under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (EA : Hex = 1 : 5) to give **1** (1.05 g, 81 %) as a brown solid. ¹H-NMR (300 MHz; DMSO-*d*₆; TMS) 10.60 (1 H, s, Ar-

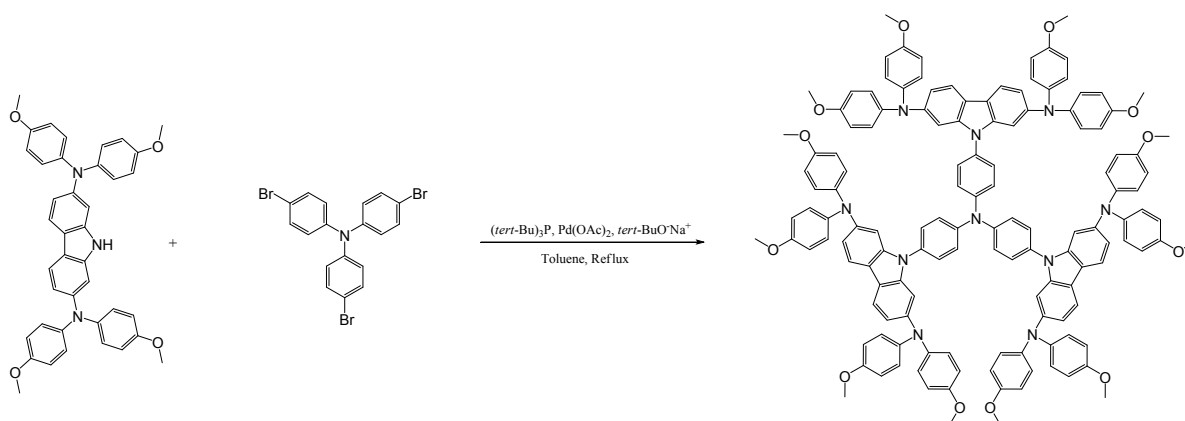
NH), 7.74 (2 H, d, $J=7.8$ Hz, Ar-H), 6.88 (16 H, m, Ar-H), 6.67 (2 H, s, Ar-H), 6.65 (2 H, d, $J=6.9$ Hz, Ar-H), 3.76 (12 H, s, Ar-OCH₃). FT-IR (KBr) [cm⁻¹] 3400 (-NH). HRMS-MS (FAB): m/z found: 621 (M⁺), calc.: 621.26.



SGT-404: **1** (2.41 g, 3.87 mmol), 4,4'-dibromo-2,2'-bis((4-(2-ethylhexyloxy)phenoxy)methyl)-6,6'-dimethylbiphenyl (1.5 g, 1.89 mmol), palladium acetate (0.08 g, 0.38 mmol), tri-tert-butylphosphine (0.15 g, 0.76 mmol) and sodium tert-butoxide (1.09 g, 11.33 mmol) dissolved in 20 ml of toluene were refluxed 5 days under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (EA : Hex = 1 : 8) to give **SGT-404** (2.5 g, 70 %) as a brown solid. ¹H-NMR (300 MHz; DMSO-d₆; TMS) 7.85 (6 H, d, $J=8.4$ Hz, Ar-H), 7.42 (2 H, s, Ar-H), 7.27 (2 H, s, Ar-H), 7.34 (16 H, d, $J=8.7$ Hz, Ar-H), 7.03 (16 H, d, $J=8.4$ Hz, Ar-H), 6.75 (8 H, s, $J=8.7$ Hz, Ar-H), 6.63 (4 H, d, $J=9.3$ Hz, Ar-H), 6.40 (4 H, d, $J=8.7$ Hz, Ar-H), 4.35 (4 H, s, Ar-CH₂O-Ar), 3.64 (24 H, s, Ar-OCH₃), 3.60 (4H, m, Ar-CH₂O-), 1.74 (6 H, s, Ar-CH₃), 1.52 (2 H, q, -CH-), 1.19 (12 H, m, -CH₂-), 0.78 (12H, m, -CH₃). ¹³C-NMR (300 MHz; DMSO-d₆; TMS) 155.39, 153.27, 151.97, 146.43, 141.02, 140.61, 137.72, 136.47, 136.03, 135.38, 126.80, 123.31, 120.04, 117.12, 115.58, 115.13, 114.66, 114.37, 101.16, 70.21, 68.57, 55.06, 54.89, 29.87, 23.19, 22.42, 18.88, 13.84, 10.79. HRMS-MS (MALDI-TOF): m/z found: 1890.22, calc.: 1890.34.



SGT-405: 1 (1.84 g, 2.95 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 5 days under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-405** (1.1 g, 60 %) as a brown solid. ¹H-NMR (300 MHz; THF-d₆; TMS) 7.87 (6 H, d, *J*=8.4 Hz, Ar-H), 7.42 (3 H, s, Ar-H), 7.06 (6 H, s, Ar-H), 6.87 (30 H, m, Ar-H), 6.47 (6 H, d, *J*=9.6 Hz, Ar-H), 3.50 (36 H, s, Ar-OCH₃). ¹³C-NMR (300 MHz; THF-d₆; TMS) 156.52, 147.39, 141.96, 140.83, 140.55, 126.33, 120.81, 119.58, 117.07, 116.12, 114.88, 114.72, 103.09, 55.37. HRMS-MS (MALDI-TOF): *m/z* found: 1937.39, calc.: 1937.23.



SGT-407: 1 (1.2 g, 1.93 mmol), tris(4-bromophenyl)amine (0.3 g, 0.62 mmol), palladium acetate (0.04 g, 0.19 mmol), tri-tert-butylphosphine (0.08 g, 0.37 mmol) and sodium tert-butoxide (0.72 g, 7.47 mmol) dissolved in 20 ml of toluene were refluxed 5 days under

nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-407** (0.7 g, 53 %) as a brown solid. ¹H-NMR (300 MHz; THF-d₆; TMS) 7.80 (6 H, d, *J*=8.1 Hz, Ar-H), 7.28 (6 H, d, *J*=8.7, Ar-H), 7.08 (6 H, d, *J*=8.7, Ar-H), 6.99 (30 H, m, Ar-H), 6.82 (6 H, m, Ar-H), 6.77 (24 H, d, *J*=9.0, Ar-H), 3.64 (36 H, s, Ar-OCH₃). ¹³C-NMR (300 MHz; THF-d₆; TMS) 155.57, 146.64, 145.92, 142.37, 141.71, 132.45, 127.49, 125.32, 124.73, 119.54, 118.36, 116.15, 114.23, 103.24, 54.51. HRMS-MS (MALDI-TOF): *m/z* found: 2104.57, calc.: 2104.44.

References

- 1 X. Cao, Y. Wen, Y. Guo, G. Yu, Y. Liu and L-M. Yang, *Dyes and Pigments*, 2010, **84**, 203
- 2 D. Sahu, C.-H. Tsai, H.-Y. Wei, K.-C. Ho, F.-C. Chang and C.-W. Chu, *J. Mater. Chem.*, 2012, **22**, 7945
- 3 A. W. Freeman, M. Urvoy and M. E. Criswell, *J. Org. Chem.*, 2005, **70**, 5014 (b) D. Patra, D. Sahu, H. Padhy, D. Kekuda, C.-H. Chu and H.-C. Lin, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2010, **48**, 5479
- 4 B. Urones, R. G. Arrayás and J. C. Carretero, *Org. Lett.*, 2013, **15**, 1120
- 5 P. J. Montoya-Pelaez, Y.-S. Uh, C. Lata, M. P. Thompson, R. P. Lemieux and C. M. Crudden, *J. Org. Chem.*, 2006, **71**, 5921

Device Fabrication

As a TiO₂ compact layer, approximately 10 nm-thick Ti film was deposited on the patterned FTO glass (Pilkington, TEC8) by an RF magnetron sputtering system (A-Tech system, Korea), followed by oxidation at 500°C for 30 min in air. Porous TiO₂ layer with ~200 nm-thickness was then spin-coated at 5,000 rpm for 30 s, using a paste derived from 50 nm-sized TiO₂ nanoparticle. The coated film was then heated at 500 °C for 30 min. CH₃NH₃PbI₃ layer was deposited by two step method reported in the literature (ref). PbI₂ solution in N,N-dimethylformamide (462 mg/mL) kept at 70 °C was coated on the porous

TiO₂ films by spin coating at 6,000 rpm for 60 s. It was dried at 70 °C for 30 min, and then cooled down to room temperature. The film was then immersed in a CH₃NH₃PbI₃ 2-propanol solution (10 mg/mL) for 20 s, and washed by 2-propanol, followed by drying at 70 °C for 15 min. As HTM layer, each of SGT-404, SGT-405, SGT-407, or spiro-MeOTAD [2,29,7,79-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene] was coated by spin-coating at 5,000 rpm for 30 s. Composition of the HTM, used for spin coating, was 111.5 mg of SGT-404 (114.3 mg for SGT-405, 124.2 mg for SGT-407, or 72.3 mg for spiro-MeOTAD) in 1 mL of chlorobenzene, 28.8 μL of 4-tert-butylpyridine, 17.5 μL of lithium bis(trifluoromethylsulphonyl) imide in 1 mL of acetonitrile, and 29 μL of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) bis(trifluoromethylsulphonyl) imide in 1 mL acetonitrile. Au layer with a thickness of 60 nm was deposited by thermal evaporator (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 cm².

Device Characterization

The morphologies of the prepared TiO₂ films were examined by field-emission scanning electron microscopy (SEM, Hitachi S4300). Photocurrent–voltage (I–V) measurements were performed 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 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. Impedance parameters were determined by fitting of the impedance spectra using Z-view software. The incident photon to current efficiency (IPCE) spectra was measured as a function of wavelength from 350 to 850 nm using a specially designed IPCE system (PV Measurements, Inc.). UV-vis absorption spectra of the HTMs in solution were measured by a shimadzu UV-2401PC spectrophotometer.

For the electrochemical measurements, cyclic voltammetry (CV) measurements were carried out with *VersaSTAT3* (AMETEK) using a typical three electrode electrochemical cell in a solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte in water-free THF at a scan rate of 50 mVs⁻¹ at room temperature; the sample was degassed with argon gas for 10 min prior to the scan. Potentials were calibrated with reference to the Fc⁺/Fc couple.

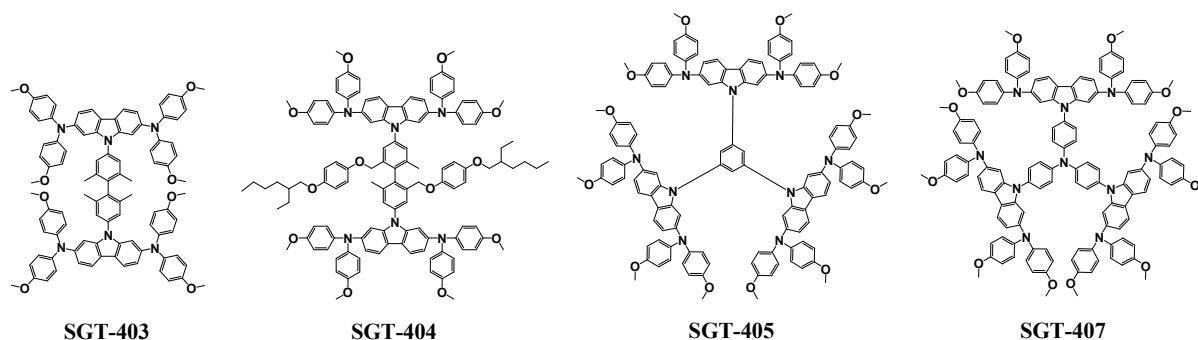
For the conductivity measurement, substrates used for two-probe electrical conductivity measurements consisted of boron-silicate glass substrate on which 40 nm Au electrodes were deposited with shadow mask patterned to yield a channel length and width of 100 μm and 500 μm , respectively. As a cleaning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

EIS measurements for the perovskite solar cells were performed using an impedance analyzer (compactstat, IVIUM Tech.). A dc potential bias was applied and overlaid by a sinusoidal ac potential perturbation of 10 mV over a frequency range of 1 MHz to 0.1 Hz . The applied dc potential bias was changed by 50 mV steps from 1000 to 650 mV. The resulting impedance spectra were fitted using the Zview software (Scribner Associates Inc.).

Table S1 Photophysical and electrochemical properties of the synthesized HTMs.

HTM	Absorption λ_{\max}^a (nm) / ϵ ($M^{-1} \text{ cm}^{-1}$)	Energy levels and band gaps		
		HOMO ^b (V vs. NHE)	Band gap ^c (eV)	LUMO (V vs. NHE)
SGT-404	386 / 118074	+0.76	3.00	-2.24
SGT-405	391 / 86436	+0.75	2.99	-2.24
SGT-407	388 / 103349	+0.74	3.00	-2.26

^a Absorption spectra were measured in THF solution. ^b The oxidation potentials of dyes, indicating HOMO levels, were measured in THF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) with a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$ (vs. NHE) using the ferrocene/ferrocenium standard. ^c Band gap was derived from the onset of absorption spectra.

**Fig. S1** Chemical structures of the synthesized SGT-series HTMs in our laboratory. SGT-404, SGT-405 and SGT-407 showed proper solubility to chlorobenzene solvent which is conventionally used for preparing spin-coating solution.

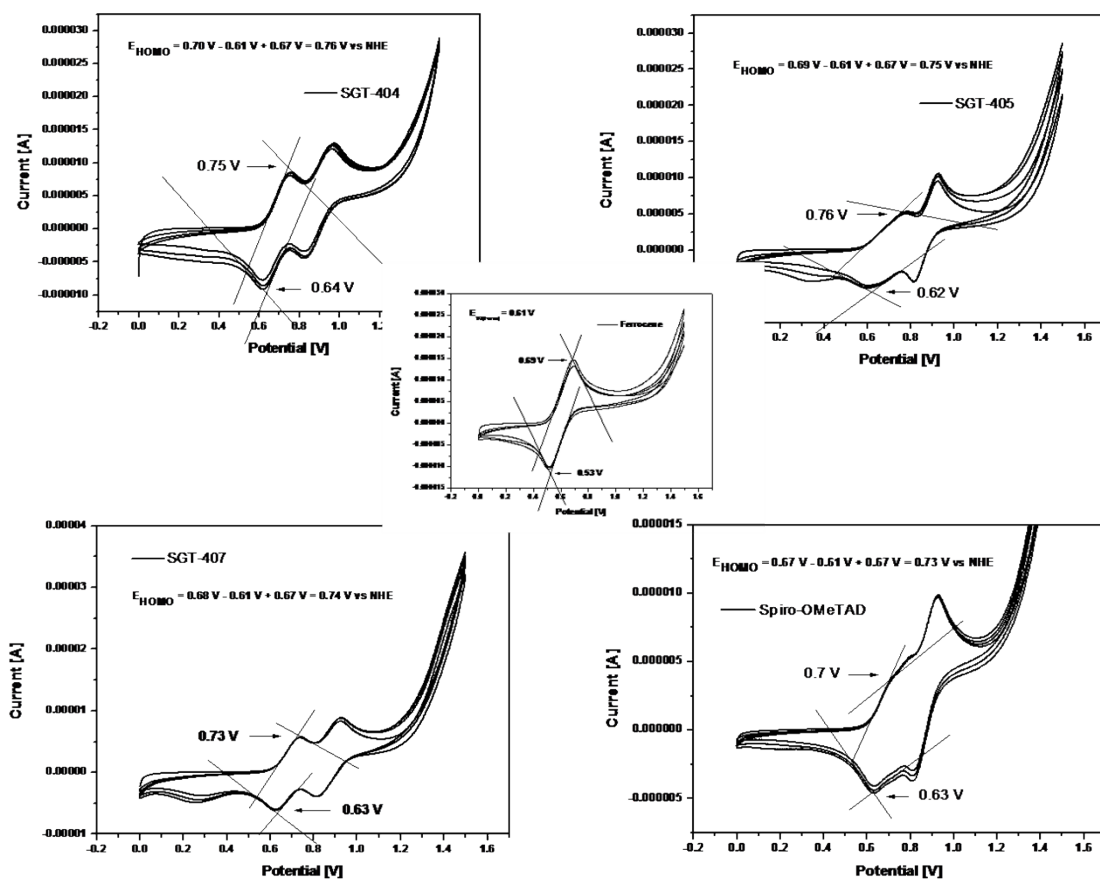


Fig. S2 Cyclic voltammograms of HTMs including spiro-OMeTAD and the FC/FC⁺ redox couple in THF with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte with scan rate of 50 mV sec⁻¹.

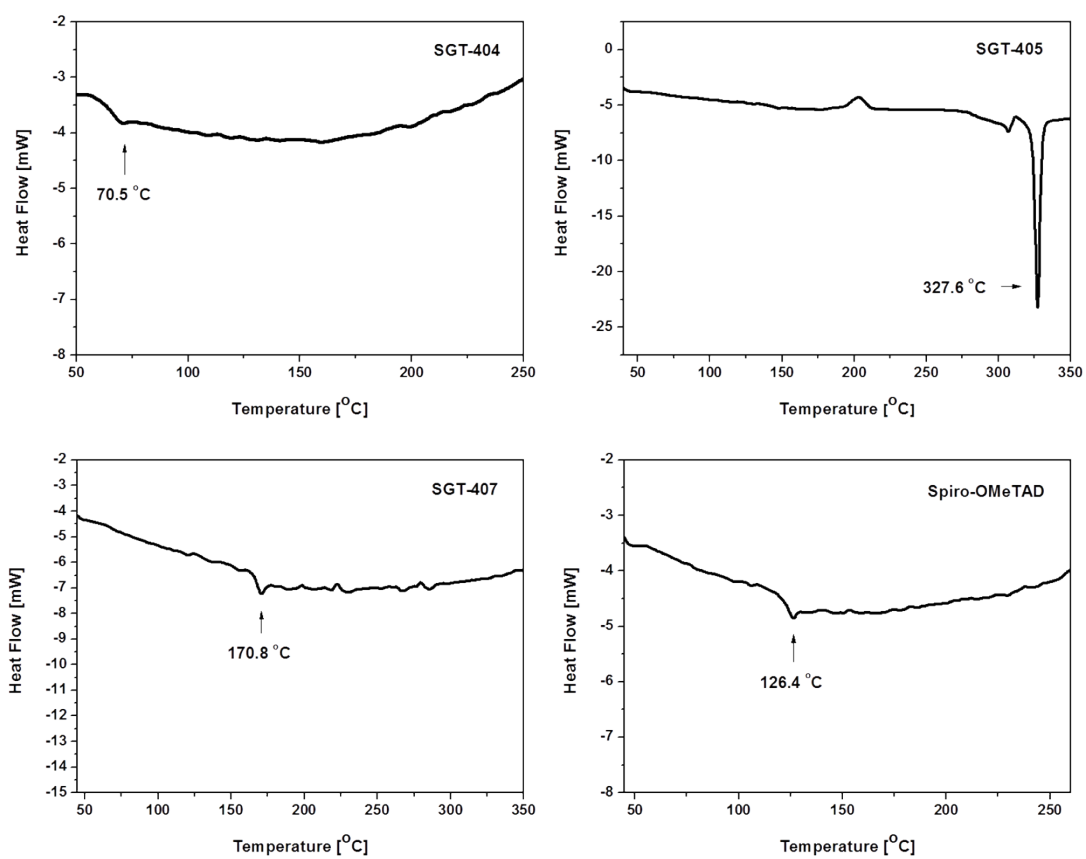


Fig. S3 Differential scanning calorimetry of HTMs including spiro-OMeTAD with scan rate of 20 °C min⁻¹. All data were collected from the second cycle of DSC curve.

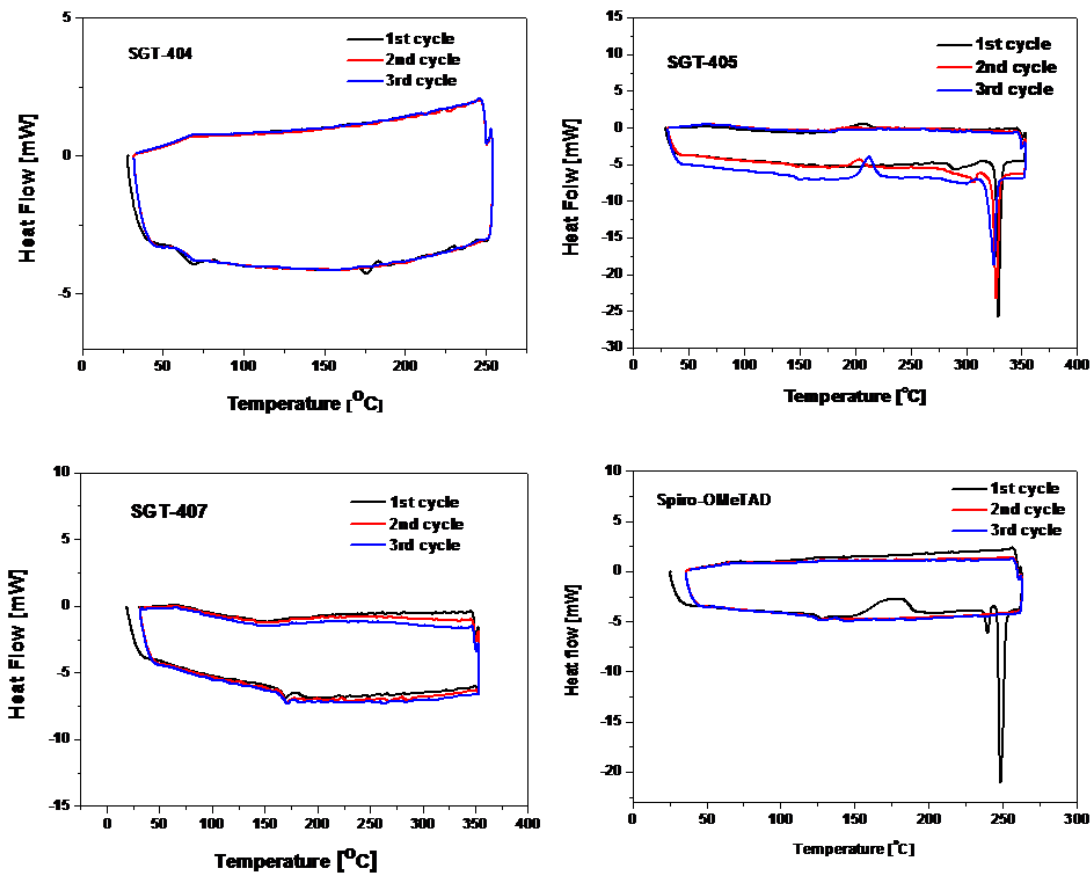


Fig. S4 Differential scanning calorimetry of HTMs including spiro-OMeTAD with scan rate of 20 °C min⁻¹.

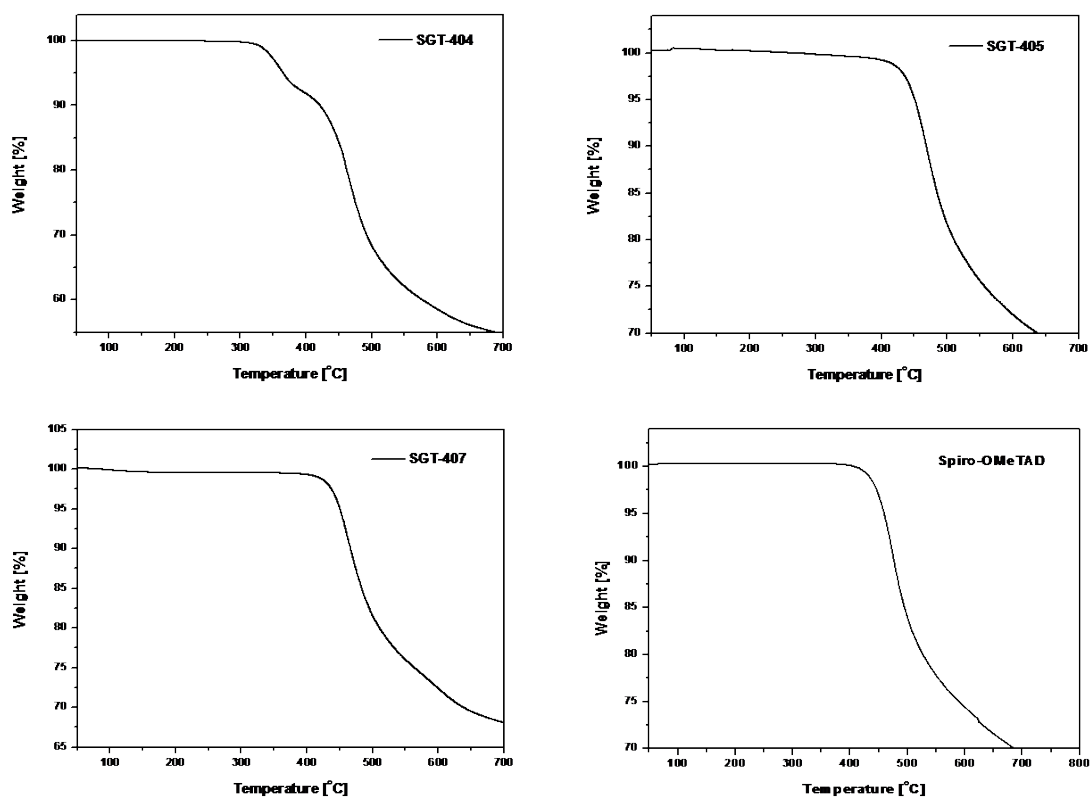


Fig. S5 Thermogravimetric analysis of HTMs including spiro-OMeTAD with scan rate of 15 °C min⁻¹.