Supporting Information

Carbazole Dendronized Triphenylamines as Solution-Processed High T_g Amorphous Hole-Transporting Materials for Organic Electroluminescent Devices

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1. General Procedures

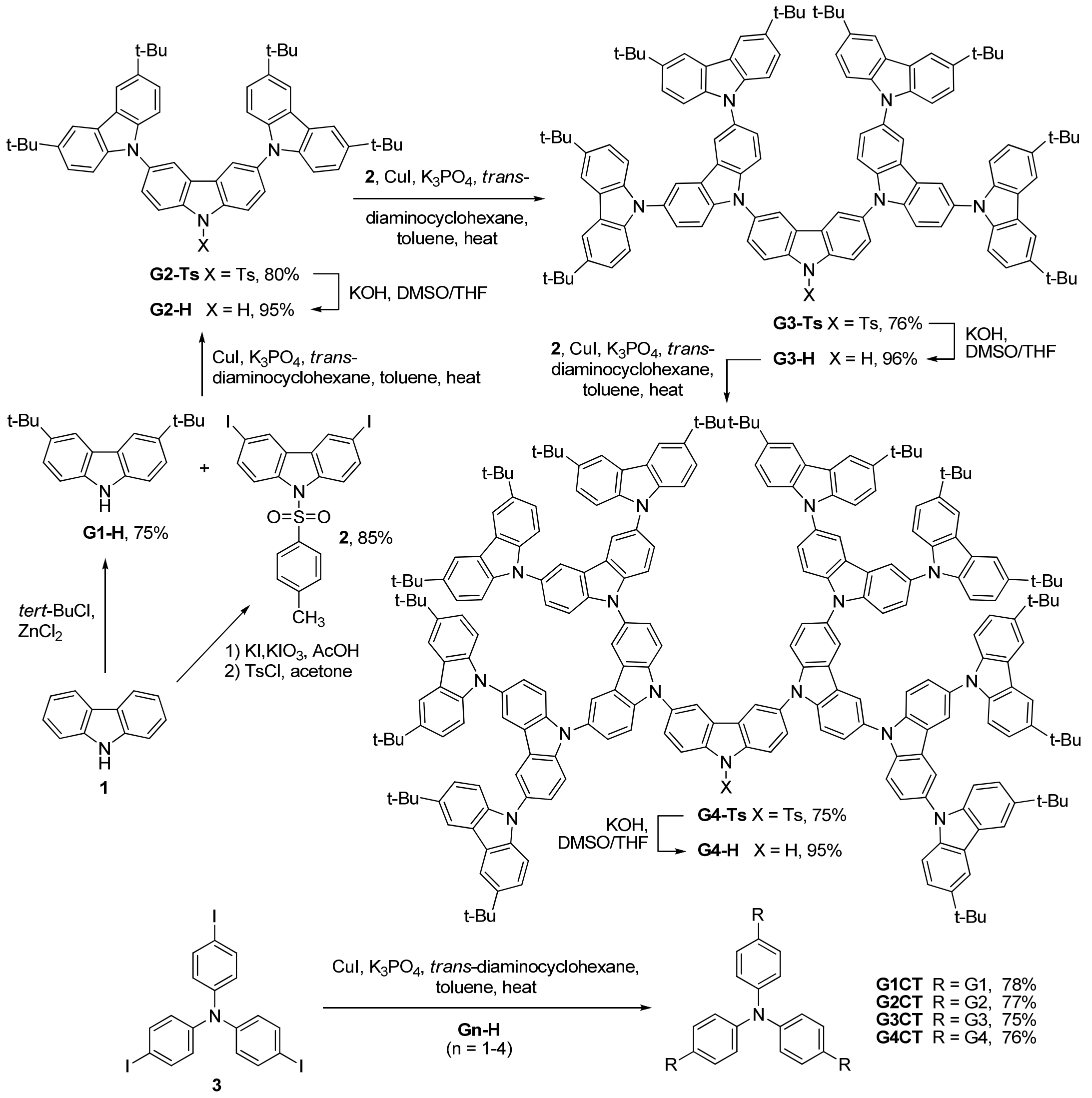
All reagents were purchased from Aldrich, Acros or Fluka and used without further purification. All solvents were supplied by Thai companies and used without further distillation. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. Dichloromethane for cyclic voltammetry (CV) measurements was washed with conc. H_2SO_4 and distilled twice from calcium hydride. Chromatographic separations were carried out on silica gel Merk Silica gel 60 (0.0630-0.200 mm).

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brüker AVANCE 300 MHz spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent in all cases. Infrared (IR) spectra were measured on a Perkin-Elmer FTIR spectroscopy spectrum RXI spectrometer as KBr disc. Ultraviolet-visible (UV-Vis) spectra were recorded as a diluted solution in spectroscopic grade dichloromethane on a Perkin-Elmer UV Lambda 25 spectrometer. Photoluminescence spectra and the fluorescence quantum yields (Φ_F) were recorded with a Perkin-Elmer LS 50B Luminescence Spectrometer as a dilute solution in spectroscopic grade dichloromethane and thin film obtained by spin casting. The fluorescence quantum yields (Φ_F) were determined by comparison with a fluorescence standard of quinine sulfate solution in 0.01 M H_2SO_4 ($\Phi_F = 0.54$).[1] Differential scanning carolimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a METTLER DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, with heating rate of 10 ^oC/min under nitrogen atmosphere. Cyclic voltammetry (CV) measurements were carried out on an Autolab potentiostat PGSTAT 12 with a three electrode system (platinum counter electrode, glassy carbon working electrode and Ag/Ag^+ reference electrode) at scan rate of 50 mV/s in dichloromethane under argon atmosphere. The concentration of analytical materials and tetrabutyl ammonium hexafluorophosphate (n-Bu_4NPF_6) were 10^{-3} M and 0.1 M, respectively. Melting points were measured using an Electrothermal IA 9100 series of digital melting point instrument and are uncorrected.

MALDI-TOF mass spectra were recorded on Bruker Daltonics (Bremen, Germany) Autoflex II Matrix-Assisted Laser Desoprtion/Ionization-Time of Flight Mass Spectrometer (BIFEX) using α-cyano-4-hydroxycinnamic acid as matrix at Chulalongkorn University. The atomic force microscopy (AFM) analysis was performed on SPA 4000 STM/AFM system using standard tipping mode with resonance of 222.223 KHz, force constant of 6.1 (+-20%), cantilever length of 87 (+-5μm), cantilever width of 32 (+-5μm), scan area of 3-5 μm and scan speed of 1Hz. Powder X-ray diffraction (XRD) was analyzed by a PHILIPS X´Pert-MDP X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å) at 1,400 W, 40 kV and 35 mA in the scanning angle (2 theta) of 10-40° with resolution of 0.04° at counting step of 1 s/step. The samples were placed on silicon wafer substrate.

2. Synthesis and Characterization

The synthesis of carbazole dendrons (**Gn-H**) and their triphenylamine dendrimers (**GnCT**) is outlined in Scheme S1.



Scheme 1. Synthetic route to carbazole dendrons (**Gn-H**) and dendrimers (**GnCT**)

Synthesis of G1-H: 3,6-Di-*tert*-butylcarbazole (**G1-H**) was prepared by adopting the literature procedure. To a stirred solution of carbazole (10.00 g, 59.80 mmol) and zinc chloride (24.45 g, 179.41 mmol) in nitromethane was added *tert*-butylchloride (19.77 ml, 179.41 mmol) under N_2 atmosphere. The solution was sonicated at room temperature for 3h. The mixture was added with water (100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic layer was washed with water (100 ml), neutralized with sodium carbonate solution, brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and removal of the solvent to dryness. Purification by recrystallization from dichloromethane and hexane gave a white powder (15.37 g, 92%). m.p. 217-219 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.47 (s, 18H; CH_3), 7.34 (d, $J = 8.5$ Hz, 2H; ArH), 7.48 (dd, $J = 8.5$ Hz, $J = 1.6$ Hz, 2H; ArH), 7.87 (s, 1H; Ar-NH), 8.11 (s, 2H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 32.12, 34.56, 110.12, 116.21, 123.32, 123.58, 138.07, 142.27. IR (KBr disc, cm^{-1}), 3419 (s (N-H 2^{o}-amine)), 3045 (s (=C-H aromatic)), 2861-2993 (s (CH_3)), 1493-1651 (s (C=C aromatic)), 1363, 1300, 1296 (vs (C-N aromatic)), 1264, 1202, 1137, 1102, 1034, 922, 880 (w (N-H (2^{o}-amine)), 818 (vs (=C-H aromatic)), 617. MALDI-TOF (m/z) (M^+) calcd for $C_{20}H_{25}N$: 279.1987, found: 278.167.

Synthesis of 2: To a solution of 3,6-diiodocarbazole (10 g, 59.80 mmol) and KOH (24.45 g, 179.41 mmol) in acetone (150 ml) under N_2 atmosphere was added slowly with *p*-toluenesulfonylchloride (24.45 g, 179.41 mmol). The reaction mixture was heated at reflux for 15 min. The reaction solution was poured into water (100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic phase was washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and removal of the solvent to dryness. Purification by recrystallization with dichloromethane and hexane gave a yellow powder (12.31 g, 90%). m.p. > 250 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.30 (s, 3H; CH_3), 7.15 (d, *J* = 8.4 Hz, 2H; ArH), 7.66 (d, *J* = 8.4 Hz, 2H; ArH), 7.79 (dd, *J* = 9 Hz, *J* = 1.5 Hz, 2H; ArH), 8.09 (d, *J* = 9 Hz, 2H; ArH), 8.17 (s, 2H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.55, 32.02, 87.96, 116.97, 126.46, 127.17, 129.15, 129.90, 134.45, 136.54, 137.81, 145.48. IR (KBr disc, cm^{-1}), 3045(s (=C-H aromatic)), 2865-2958 (s (CH_3)), 1493-1594 (s (C=C aromatic)),1465, 1423, 1362 (vs (C-N aromatic)),1207, 1188, 1169 (s (S=O)), 1130, 1090,1020, 967, 819, 711(vs (=C-H aromatic)), 588, 571,533 (s (C-I)). MALDI-TOF (m/z) (M^+) calcd for $C_{19}H_{13}I_2NO_2S$: 572.8756, found: 572.280.

Synthesis of G2-Ts: A mixture of **2** (4 g, 6.98 mmol), **G1-H** (4.29 g, 15.35 mmol), K_3PO_4 (3.72 g, 17.50 mmol) and CuI (0.57 g, 3.50 mmol) in toluene (60 ml) was degassed with N_2 for 5 min followed by an addition of (±)-trans-1,2-diaminocyclohexane. The reaction mixture was heated at 110 ^{o}C for 24 h and the solvent was removed to dryness. The crude was added with and water (100 ml) and extracted with dichloromethane (2 x 100 ml). The combined organic phase was washed with water (100 ml), brine solution (100 ml), dried over anhydrous Na_2SO_4, filtered and removal of the solvent to dryness. Purification by column chromatography over silica gel eluting with a mixture of dichloromethane and hexane (1:4) followed by recrystallization with a mixture of dichloromethane and methanol afforded a white solid (4.77 g, 78%); m.p. 222-224 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.48 (s, 36H; CH_3), 2.42 (s, 3H; CH_3), 7.28-7.37 (m, 6H; ArH), 7.47 (dd, *J* = 9.0 Hz, *J* = 1.5 Hz , 4H; ArH), 7.76 (dd, *J* = 9.0 Hz, *J* = 1.8 Hz , 2H; ArH), 7.94 (d, *J* = 8.1 Hz, 2H; ArH), 8.07 (d, *J* = 1.8 Hz, 2H; ArH), 8.16 (s, 2H; ArH), 8.17 (s, 2H; ArH), 8.58 (s, 1H; ArH), 8.61 (s, 1H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.70, 32.04, 32.08, 34.77, 109.01, 109.14, 116.20, 116.34, 118.53, 123.43, 123.57, 123.73, 126.79, 127.13, 130.10, 134.58, 135.06, 137.41, 139.55, 145.51. IR (KBr disc, cm^{-1}), 3054 (s (=C-H aromatic)), 2861-2949 (s (CH_3)), 1489-1614 (s (C=C aromatic)), 1453, 1374, 1362 (vs (C-N aromatic)), 1325, 1295, 1261, 1235, 1179, 1169 (s (S=O)), 1132, 1092, 1033, 973, 875, 807, (vs (=C-H aromatic)), 740, 705, 667,585. MALDI-TOF (m/z) (M^+) calcd for $C_{59}H_{61}N_3O_2S$: 875.4484, found: 874.919.

Synthesis of G2-H: A mixture of **G2-Ts** (1 g, 1.14 mmol), KOH (0.13 g, 2.32 mmol), dimethylsulphoxide (6 ml), tetrahydrofuran (12 ml) and water (2 ml) was stirred at reflux temperature under N_2 atmosphere for 25 min. After the mixture was cooled to room temperature, 10% HCl (20 ml) was added, followed by water (10 ml) and methanol (5 ml). The precipitate was collected on by filtration and washed with water several times followed by recrystallization with a mixture of dichloromethane and methanol to give a white solid (0.78 g, 95%). m.p 246-248 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.48 (s, 36H; CH_3), 7.33 (d, *J* = 8.4 Hz, 4H; ArH), 7.47 (d, *J* = 8.4 Hz, 4H; ArH), 7.59 (d, *J* = 6.9 Hz, 4H; ArH), 8.18 (s, 6H; ArH), 8.45 (s, 1H; Ar-NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ)

30.93, 32.06, 34.74, 109.14, 111.89, 116.19, 119.40, 123.09, 123.56, 124.09, 125.93, 130.44, 139.04, 140.22, 142.53. IR (KBr disc, cm^{-1}), 3450 (s (N-H 2^{o}-amine)), 3046 (s (=C-H aromatic)), 2865-2958 (s (CH_3)), 1493-1627 (s (C=C aromatic)),1363, 1325, 1292 (vs (C-N aromatic)),1262, 1236, 1168, 1033, 875 (w (N-H (2^{o}-amine)), 809 (vs (=C-H aromatic)), 741, 655, 611, 570. MALDI-TOF (m/z) (M^+) calcd for $C_{52}H_{55}N_3$: 721.4396, found: 720.876.

Synthesis of G3-Ts: G3-Ts was prepared in similar manner to **G2-Ts** from **G2-H** (4.29 g) and **2** (4 g), and obtained as a white solid (9.34 g, 76%). m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.51 (s, 72H; CH_3), 2.46 (s, 3H; CH_3), 7.37-7.42 (m, 10 H; ArH), 7.50 (d, *J* = 8.4 Hz, 9H; ArH), 7.66 (s, 8H; ArH), 8.01 (d, *J* = 8.7 Hz, 2H; ArH), 8.07 (d, *J* = 8.1 Hz, 2H; ArH), 8.20 (s, 8H; ArH), 8.31 (s, 4H; ArH), 8.42 (s, 2H; ArH), 8.81 (d, *J* = 9.0 Hz, 2H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 21.78, 32.09, 34.78, 76.64, 77.06, 77.48, 109.10, 110.98, 116.29, 116.79, 119.52, 123.19 123.62, 124.07, 126.16, 127.92, 127.16, 127.51, 131.15, 130.30, 133.61, 138.24, 140.18, 140.18, 142.66, 145.90. IR (KBr disc, cm^{-1}), 3046 (s (=C-H aromatic)), 2861-2949 (s (CH_3)), 1489-1629 (s (C=C aromatic)),1379,1362 (vs (C-N aromatic)),1324, 1295, 1281, 1262, 1231, 1187, 1175 (s (S=O)), 1131, 1033, 875, 807, (vs (=C-H aromatic)), 741, 689, 664, 611, 585, 543. MALDI-TOF (m/z) (M^+) calcd for $C_{123}H_{121}N_7O_2S$: 1759.9302, found: 1760.625 (M^+).

Synthesis of G3-H: G3-H was prepared in similar manner to **G2-H** from **G3-Ts** (1 g), and obtained as a white solids (0.65 g, 95%). m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.46 (s, 72H; CH_3), 7.35 (d, *J* = 8.4 Hz, 8H; ArH), 7.46 (dd, *J* = 9.0 Hz, *J* = 1.8 Hz, 8H; ArH), 7.61 (s, 8H; ArH), 7.84 (s, 4H; ArH), 8.16 (s, 4H; ArH), 8.17 (s, 4H; ArH), 8.27 (s, 4H; ArH), 8.47 (s, 2H; ArH), 8.65 (s, 1H; Ar-NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 32.05, 34.73, 109.12, 111.08, 112.47, 116.20, 123.09, 123.55, 123.74, 124.27, 125.99, 126.35129.60, 130.69, 139.68, 140.21, 142.52. IR (KBr disc, cm^{-1}), 3424 (s (N-H 2^{o}-amine)), 3046 (s (=C-H aromatic)), 2865-2958 (s (CH_3)), 1487-1631 (s (C=C aromatic)),1363, 1325, 1294 (vs (C-N aromatic)), 1280, 1263, 1235, 1034, 875 (w (N-H (2^{o}-amine)), 809 (vs (=C-H aromatic)), 714, 668, 655, 611. MALDI-TOF (m/z) (M^+) calcd for $C_{116}H_{115}N_7$: 1605.9214, found: 1606.277.

Synthesis of G4-Ts: G4-Ts was prepared in similar manner to **G1-Ts** from **G3-H** (2.46 g) and **2** (0.41 g), and obtained as a white solids (1.89 g, 75%). m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.51 (s, 144H; CH_3), 2.53 (s, 3H; CH_3), 7.40 (d, *J* = 8.1 Hz, 17H; ArH), 7.50 (d, *J* = 7.2 Hz, 17H; ArH), 7.69 (d, *J* = 4.2 Hz, 16H), 7.86 (d, *J* = 8.4 Hz, 4H; ArH), 7.93 (d, *J* = 8.7 Hz, 4H; ArH), 8.09-8.17 (m, 4H; ArH), 8.22 (s, 16H; ArH), 8.34 (s, 8H; ArH), 8.59 (s, 2H; ArH), 8.66 (s, 4H; ArH), 8.93 (d, *J* = 8.7 Hz, 2H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 10.95, 14.02, 22.97, 23.78, 28.94, 29.34, 29.69, 30.39, 31.61, 32.01, 34.69, 38.77, 68.18, 109.07, 111.03, 111.67, 116.17, 119.41, 120.06, 123.11, 123.52, 123.78, 123.94, 126.01, 128.80, 129.93, 130.86, 140.20, 141.39, 142.12, 142.51. IR (KBr disc, cm^{-1}), 3046 (s (=C-H aromatic)), 2865-2953 (s (CH_3)), 1487-1629 (s (C=C aromatic)), 1391, 1380, 1364 (vs (C-N aromatic)), 1324, 1295, 1281, 1262, 1231, 1187, 1173 (s (S=O)), 1104, 1090, 1033, 970, 920, 875 (vs (=C-H aromatic)), 838,, 808, 740, 689, 663, 610, 584, 543 . MALDI-TOF (m/z) (M^+) calcd for $C_{251}H_{241}N_{15}O_2S$: 3528.8938, found: 3531.1599.

Synthesis of G4-H: G4-H was prepared in similar manner to **G2-H** from **G4-Ts** (1 g) and obtained by purification with by column chromatography over silica gel eluting with a mixture of dichloromethane and hexane (1:4) to give a white solid (0.91 g, 95%). m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.45 (s, 144H; CH_3), 7.34 (d, *J* = 8.4 Hz, 16 H; ArH), 7.45 (d, *J* = 8.4 Hz, 16 H; ArH), 7.61 (d, *J* = 8.4 Hz, 8H; ArH), 7.67 (d, *J* = 8.4 Hz, 8H; ArH), 7.90-7.94 (m, 12H; ArH),8.16 (s, 16H; ArH), 8.28 (s, 8H; ArH), 8.60 (s, 4H; ArH), 8.63 (s, 2H; ArH),8.73 (s, 1H; Ar-NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 32.05, 34.74, 109.30, 116.23, 123.37, 123.57, 127.77, 139.37, 142.91. IR (KBr disc, cm^{-1}), 3410 (s (N-H 2°-amine)), 3046 (s (=C-H aromatic)), 2852-2953 (s (CH_3)), 1484-1629 (s (C=C aromatic)), 1391, 1362, 1324, 1294 (vs (C-N aromatic)), 1280, 1262, 1233, 1153, 1130, 1033, 875 (w (N-H (2°-amine)), 805 (vs (=C-H aromatic)), 740, 655, 610, 571, 503. MALDI-TOF (m/z) (M^+) calcd for $C_{244}H_{235}N_{15}$: 3374.8850, found: 3376.830.

Synthesis of G1CT: A mixture of **3** (0.30 g, 0.48 mmol), **G1-H** (0.67 g, 2.40 mmol), K_3PO_4 (0.38 g, 1.82 mmol) and CuI (0.14 g, 0.72 mmol) in toluene (30 ml) was stirred and degassed with N_2 for 5 min followed by an addition of (±)-*trans*-1,2-diaminocyclohexane. The reaction mixture was heated at 110 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtrated through a plug of silica gel washing with dichloromethane. After the solvent was evaporated to dryness, the residue was purified by column chromatography over silica gel eluting with a mixture of dichloromethane and hexane (1:4) followed by recrystallization with a mixture of dichloromethane and methanol to give a white solid (0.40 g, 78%). m.p. 228-230 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.48 (s, 54H; CH_3), 7.48-7.58 (m, 24H; ArH), 8.19 (s, 6H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 21.78, 32.09, 34.78, 76.64, 77.06, 77.48, 109.10, 110.98, 116.29, 116.79, 119.52, 123.19, 123.62, 124.07, 126.16, 127.92, 127.16, 127.51, 130.30, 131.15, 133.61, 138.24, 140.18, 142.66, 145.90. IR (KBr disc, cm^{-1}), 3041 (s (=C-H aromatic), 2861-2953 (s (CH_3)), 1504-1627 (s (C=C aromatic)),1487, 1472, 1392, 1363, 1313, 1292 (vs (C-N aromatic)), 1262, 1232, 1193, 1103, 1033, 875 (vs (=C-H aromatic)), 808, 741, 652, 610, 597, 533. UV-Vis (dichloromethane) λ_{max} (ε, 10^5 dm^{3}mol^{-1}cm^{-1}) 298 nm (2.76), 326 nm (2.07). MALDI-TOF (m/z) (M^+) calcd for $C_{78}H_{84}N_4$: 1076.6696, found: 1076.131.

Synthesis of G2CT: G2CT was prepared in similar manner to **G1CT** from **3** (0.07 g, 0.12 mmol) and **G2-H** (0.45 g, 0.62 mmol), and obtained as a white solid (0.20 g, 77%). m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.48 (s, 108H; CH_3), 7.36 (d, *J* = 8.7 Hz, 12H; ArH), 7.49 (d, *J* = 8.4 Hz, 12H; ArH), 7.66-7.84 (m, 24H; ArH), 8.18 (s, 12H; ArH), 8.26 (s, 6H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 32.04, 34.74, 109.06, 111.15, 116.25, 119.42, 123.17, 123.57, 124.03, 125.75, 126.03, 128.57, 131.04, 132.67, 140.16, 140.52, 142.63, 146.88. IR (KBr disc, cm^{-1}), 3046 (s (=C-H aromatic), 2865-2953 (s (CH_3)), 1504-1629 (s (C=C aromatic)), 1484, 1392, 1363, 1315, 1292 (vs (C-N aromatic)), 1280, 1262, 1233, 1162, 1104, 1033, 875 (vs (=C-H aromatic)), 839, 807, 740, 655, 610, 568. UV-Vis (dichloromethane) λ_{max} (ε, 10^5 dm^{3}mol^{-1}cm^{-1}) 298 nm (2.34), 326 nm (1.17). MALDI-TOF (m/z) (M^+) calcd for $C_{174}H_{174}N_{10}$:2403.3923, found: 2403.405

Synthesis of G3CT: G3CT was prepared in similar manner to **G1CT** from **3** (0.02 g, 0.03 mmol) and **G3-H** (0.50 g, 0.14 mmol), and obtained as a white solid (0.12 g, 75%). m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.48 (s, 216H; CH_3), 7.36 (d, *J* = 7.2 Hz, 22H; ArH), 7.47 (d, *J* = 8.1 Hz, 26H; ArH), 7.66 (d, *J* = 3.9 Hz, 24H; ArH), 7.90-7.98 (m, 24H; ArH), 8.18 (s, 24H; ArH), 8.30 (s, 12H; ArH), 8.62 (s, 6H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 29.72, 32.05, 34.74, 109.08, 111.01, 111.74, 116.25, 119.50, 120.21, 123.15, 123.56, 123.86, 124.28, 125.97, 126.08, 126.52, 128.82, 130.27, 130.88, 132.56, 140.21, 141.24, 141.37, 124.60, 147.17. IR (KBr disc, cm^{-1}), 3046 (s (=C-H aromatic), 2861-2953 (s (CH_3)), 1489-1629 (s (C=C aromatic)), 1391, 1362, 1323, 1259 (vs (C-N aromatic)), 1230, 1181, 1103, 871 (vs (=C-H aromatic)), 807, 740, 655, 610. UV-Vis (dichloromethane) λ_{max} (ε, 10^5 dm^{3}mol^{-1}cm^{-1}) 298 nm (3.8389), 326 nm (1.3383). MALDI-TOF (m/z) (M^+) calcd for $C_{366}H_{354}N_{22}$:5056.8377, found: 5058.529.

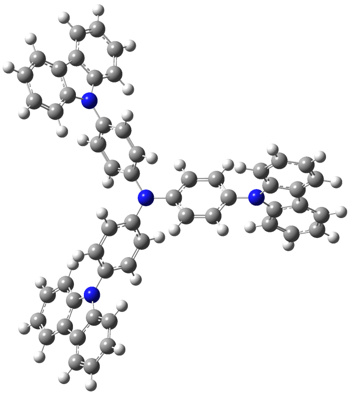
Synthesis of G4CT: G4CT was prepared in similar manner to **G1CT** from **3** (0.015 g, 0.03 mmol)) and **G4-H** (0.50 g, 0.14 mmol), and obtained as a white solid (230 mg, 76%). m.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.47 (s, 432H; CH_3), 7.33 (d, *J* = 8.4 Hz, 48H; ArH), 7.43 (d, *J* = 8.4 Hz, 48H; ArH), 7.58-7.73 (m, 60H; ArH), 7.84 (d, *J* = 8.7 Hz, 12H; ArH), 7.88 (d, *J* = 10.2 Hz, 12H; ArH), 8.02 (s, 12H; ArH), 8.15 (s, 48H; ArH), 8.27 (s, 24H; ArH), 8.60 (s, 12H; ArH), 8.72 (s, 6H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, δ); 29.72, 32.09, 34.70, 109.06, 111.00, 116.20, 119.45, 123.11, 123.53, 123.80, 126.02, 130.88, 140.18, 141.66 142.60. IR (KBr disc, cm^{-1}), 3046 (s (=C-H aromatic), 2857-2953 (s (CH_3)), 1489-1616 (s (C=C aromatic)), 1362, 1324, 1294, 1261 (vs (C-N aromatic)), 1232, 1098, 1022, 920, 876 (vs (=C-H aromatic)), 805, 740, 610. UV-Vis (dichloromethane) λ_{max} (ε, 10^5 $dm^3mol^{-1}cm^{-1}$) 298 nm (5.1547), 326 nm (1.4577). MALDI-TOF (m/z) (M^+) calcd for $C_{750}H_{714}N_{46}$: 10363.7285, found: 10436.618.

2. Computer quantum calculation results

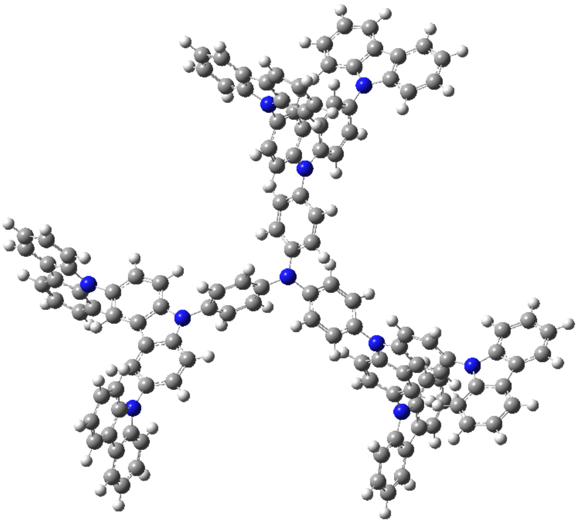
The ground state geometries of **GnCT** were fully optimized using HF/6-31G(d,p) level, as implemented in Gaussian 03.[2]

3. Device Fabrication and Testing

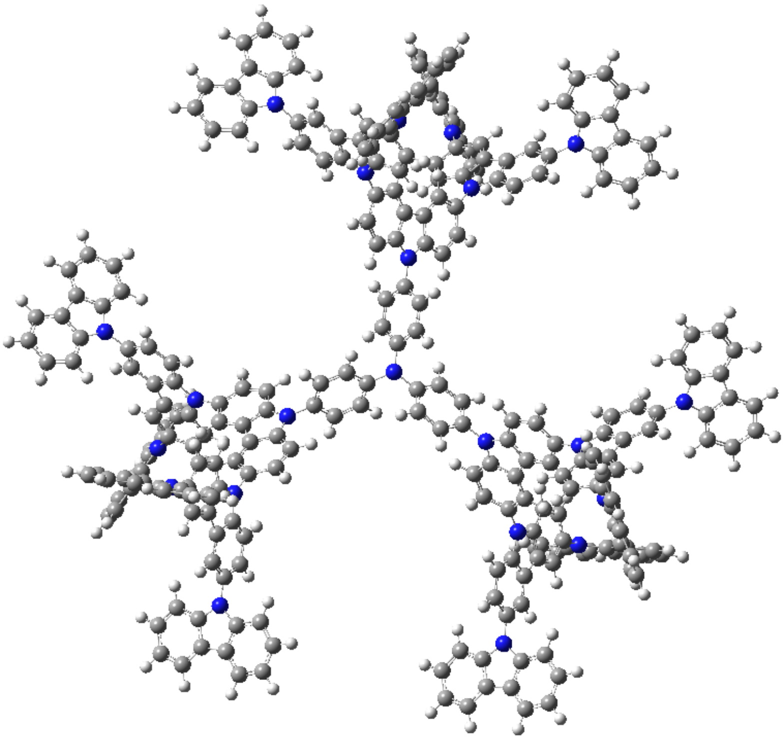
Alq3-based green OLED devices using **GnCT** and NPB as HTL with configuration ITO/PEDOT:PSS/HTL(40 nm)/Alq3(50 nm)/LiF(0.5 nm):Al(150 nm) were fabricated and characterized as followed. The patterned indium tin oxide (ITO) glass substrate with a sheet resistance 14 Ω/☐ (purchased from Kintec Company) was thoroughly cleaned by successive ultrasonic treatment in detergent, deionised water, isopropanol, and acetone, and then dried at 60 °C in a vacuum oven. A 50 nm thick PEDOT:PSS hole injection layer was spin-coated on top of ITO from a 0.75 wt.% dispersion in water at a spin speed of 3000 rpm for 20 s and dried at 200 °C for 15 min under vacuum. Thin films of HTL were deposited on top of PEDOT:PSS layer by spin-coating chloroform:toluene solution of **GnCT** and **NBP** (1.5% w/v) on an ITO glass substrate at a spin speed of 3000 rpm for 30 second to get a 40 nm thick of hole-transporting layer (HTL). The film thickness was measured by using a Tencor α-Step 500 surface profiler. Then Alq3 was deposited onto the surface of the HTL film as light-emitting (EML) and electron-transporting layer (ETL) with a thickness of 50 nm by evaporation from resistively heated alumina crucibles at evaporation rate of 0.5-1.0 nm/s in vacuum evaporator deposition (ES280, ANS Technology) under a base pressure of ~10-5 mbar. The film thickness was monitored and recorded by quartz oscillator thickness meter (TM-350, MAXTEK). The chamber was vented with dry air to load the cathode materials and pumped back; a 0.5 nm thick LiF and a 150 nm thick aluminium layers were the subsequently deposited through a shadow mask on the top of EML film without braking vacuum to from an active diode areas of 4 mm2. The measurement of device efficiency was performed according to M.E. Thomson's protocol and the device external quantum efficiencies were calculated using procedure reported previously.[3] Current density-voltage-luminescence (*J-V-L*) characteristics were measured simultaneous by the use of a Keithley 2400 source meter and a Newport 1835C power meter equipped with a Newport 818-UV/CM calibrated silicon photodiode. The EL spectra were acquired by an Ocean Optics USB4000 multichannel spectrometer. All the measurements were performed under ambient atmosphere at room temperature.



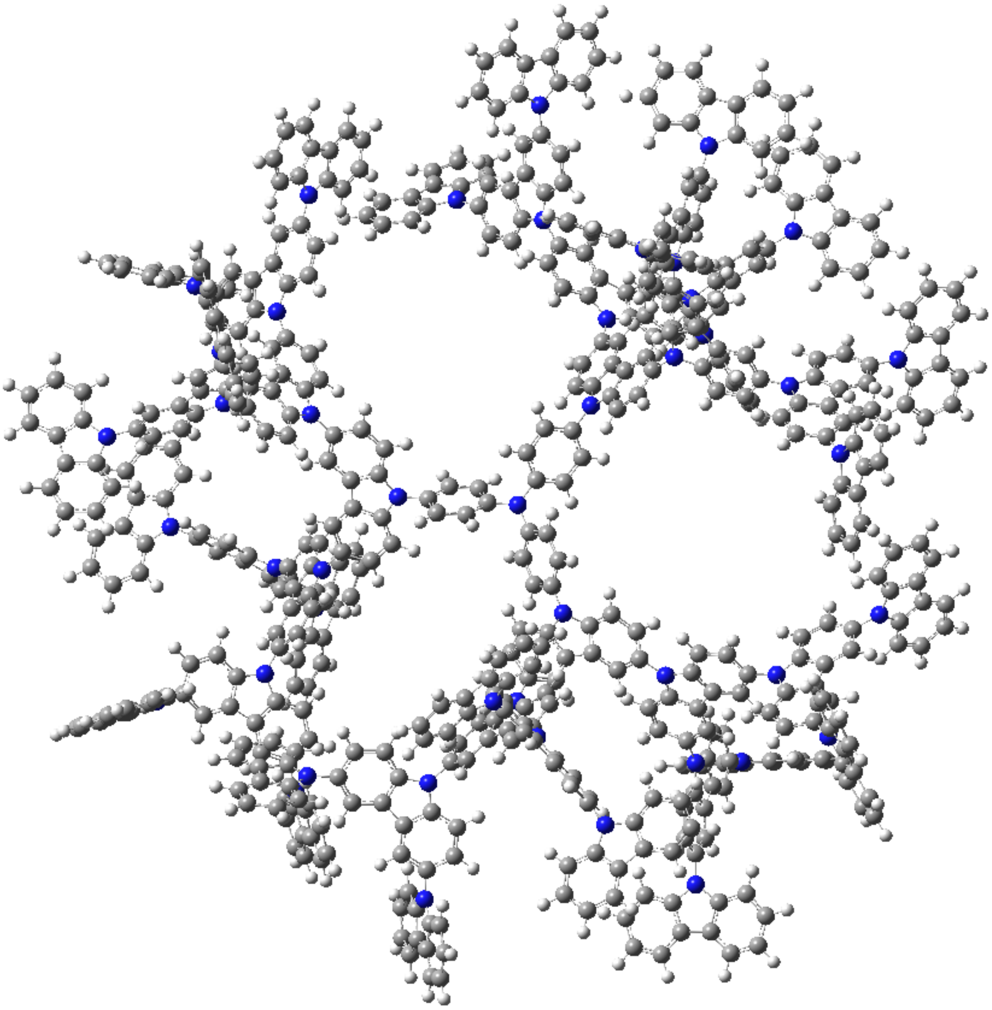
G1CT



G2CT



G3CT



G4CT

Figure S1 The optimized geometries of **GnCT** by the GIAO (Gauge-Independent Atomic Orbital) method at the HF/6-31G(d,p) level with *tert*-butyl groups are omitted.

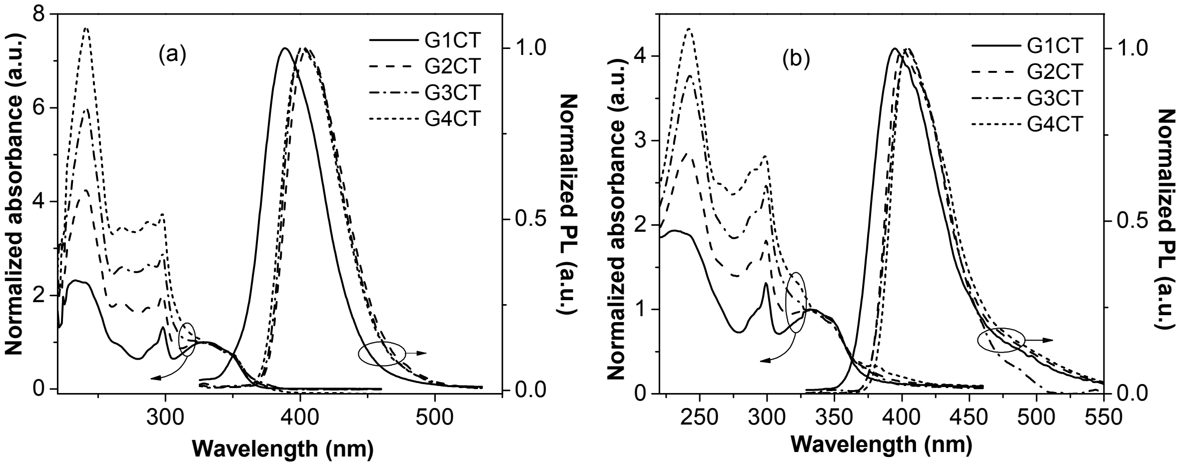


Figure S2 UV-Vis and photoluminescence (PL) spectra of **GnCT** in a) CH_2Cl_2 solution and b) thin film obtained from spin casting.

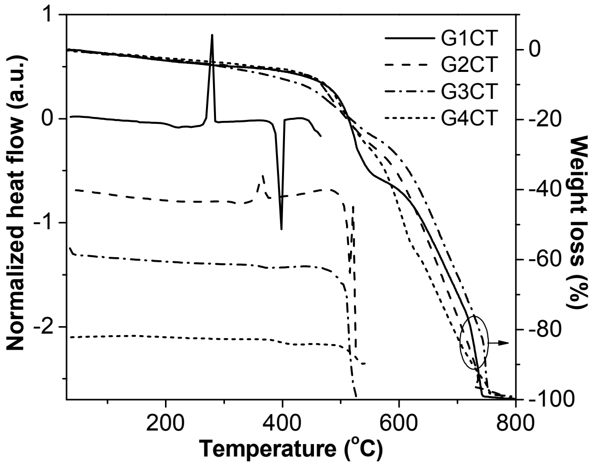


Figure S3 DSC (2nd heating scan) and TGA curves of **GnCT** measured at 10 °C/min under N_2.

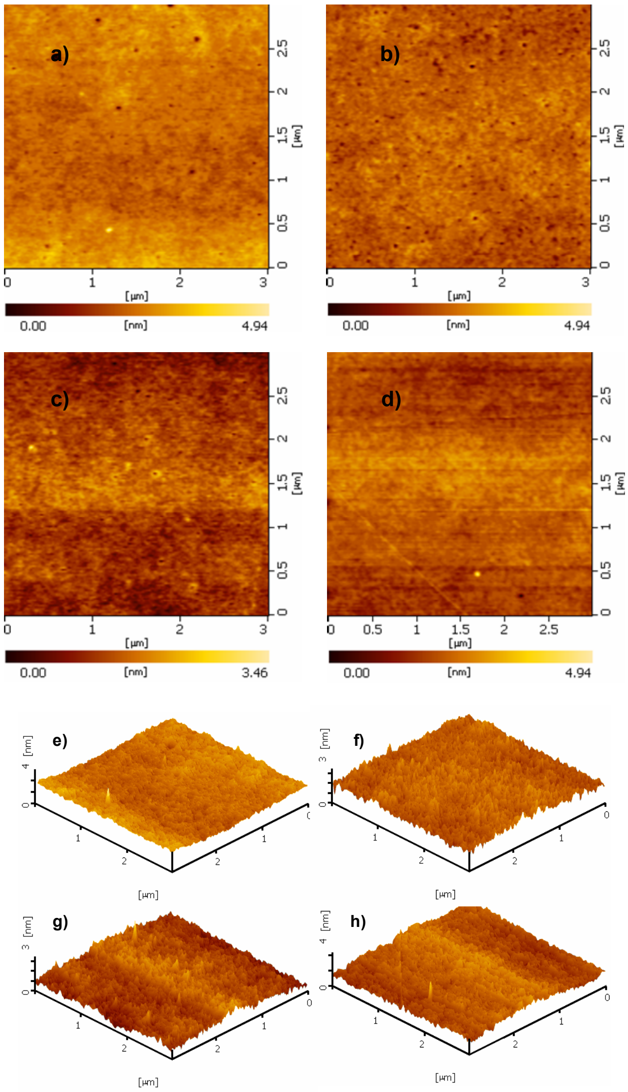


Figure S4 Tapping mode AFM images of spin-coated films: a) and e) **G1CT**; b) and f) **G2CT**; c) and g) **G3CT**; d) and h) **G4CT**

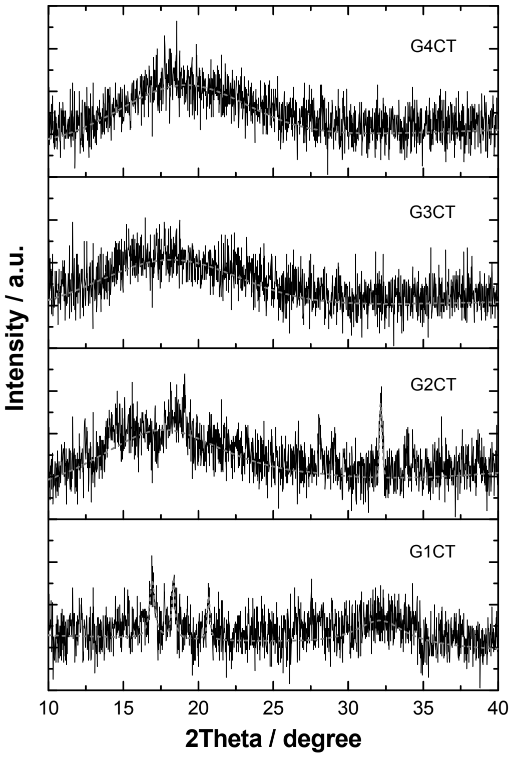
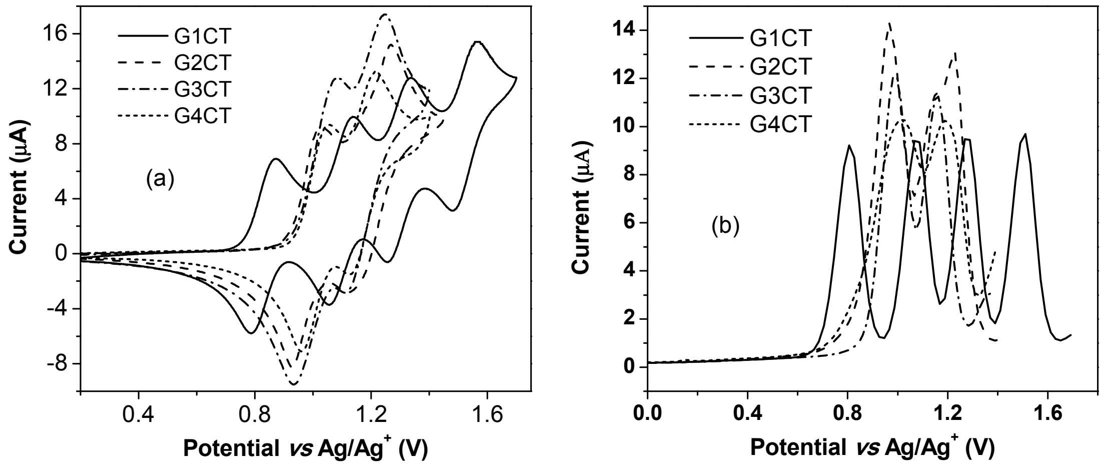


Figure S5 Powder X-ray diffraction patterns of **GnCT** on silicon substrate (dotted line represents Xfit data).



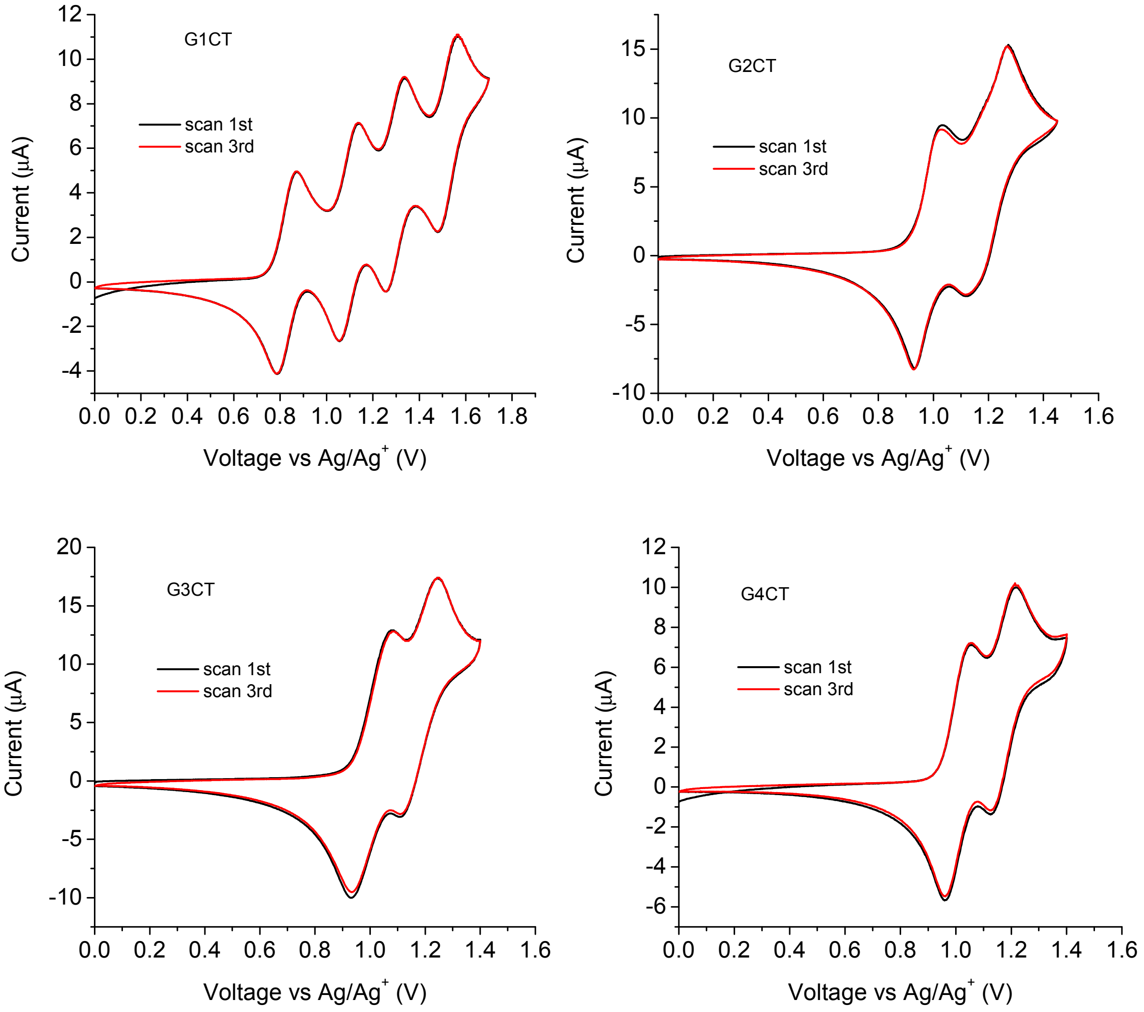


Figure S6 (a) CV and (b) DPV curves of **GnCT** measured in CH_2Cl_2 at a scan rate of 50 mV/s. (c) Multiple CV scan curves of **GnCT** measured in CH_2Cl_2 at a scan rate of 50 mV/s.

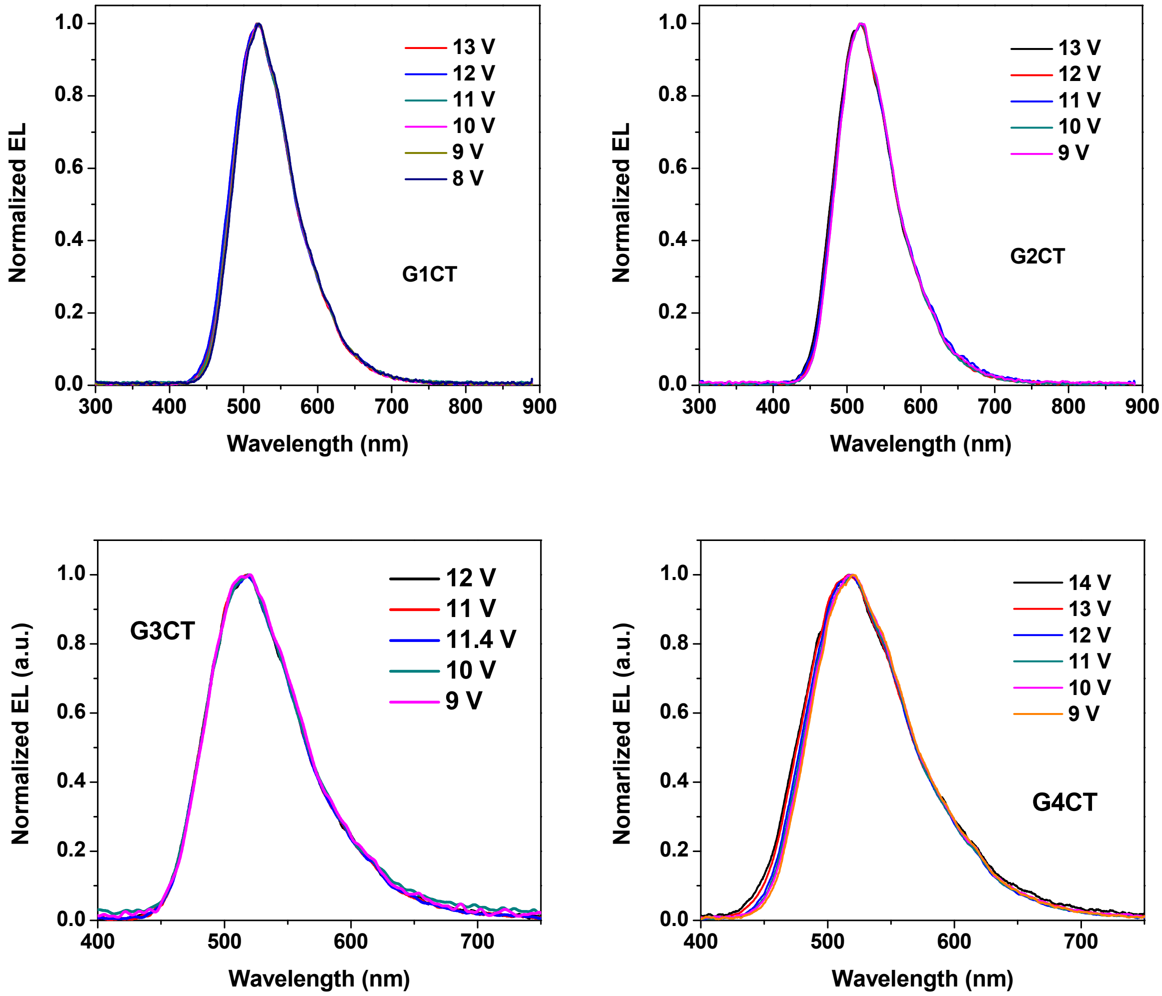


Figure S7 Normalized EL spectra of OLED devices I-IV under differnent applied voltages.

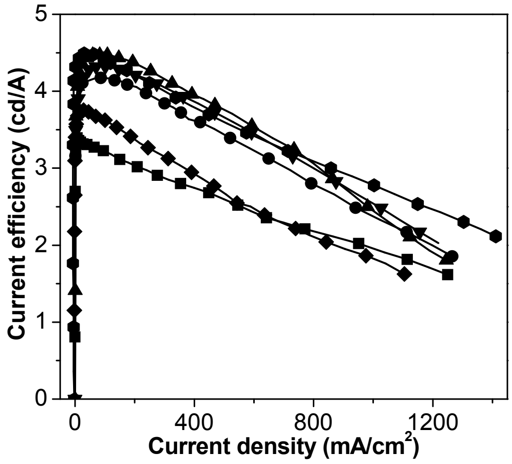


Figure S8 variation of luminance efficiency with current density of OLEDs with and without **GnCT** as HTL. Device I (■), device II (●), device III (▲up triangle), device IV (▼) and device V (★).

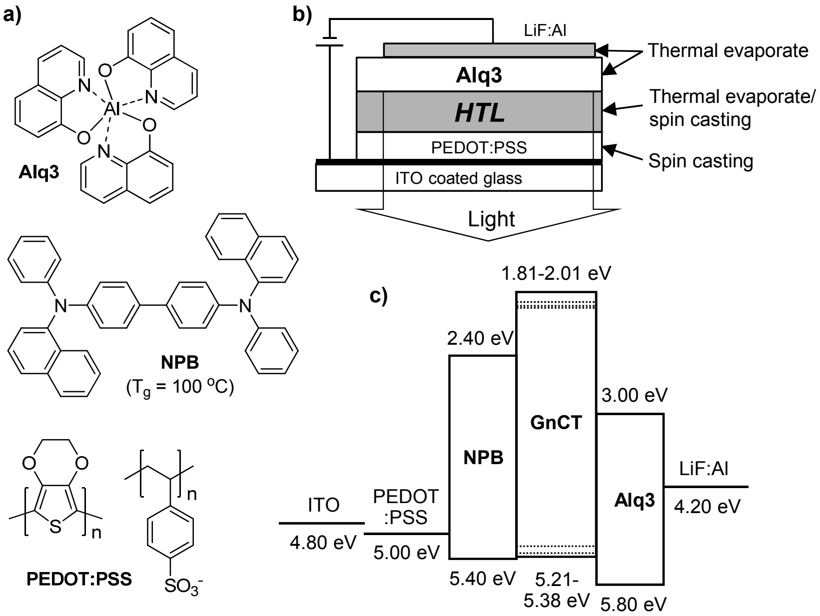


Figure S9 a) Molecular structures of the materials used in this work. b) Typical Alq3-based green OLED devices fabricated in this work. c) A schematic of the energy band diagram of each layer of the devices.

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