# Supporting Information

# Spiro-Based Hole-Transporting Materials Utilized in Green Perovskite Quantum Dot Light-Emitting Diodes with High Luminance

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## Materials Characterization

All experimental reagents which commercially available with analytical or chemical purity were purchased from Shanghai Haohong Biopharmaceutical Technology Co., Ltd.; besides, the solvent was purchased directly from commercialization to use. During the testing process, $^{1}H$ & $^{13}C$ nuclear magnetic resonance (NMR) spectra were measured via a Bruker-AM 400 spectrometer at room temperature, using deuterium chloroform as the internal standard. Mass spectrometry data were determined by high resolution mass spectrometry (XEVO-G2 TOF). The UV-visible absorption spectra (UV-Vis) were characterized using a Lambda 950 UV-visible-near-infrared spectrophotometer and the photoluminescence (PL) spectra were recorded at room temperature with an Agilent Cary Eclipse spectrometer. Thermogravimetric analysis (TGA) was performed by a Shimadzu TGA-50/50H thermal gravimetric analyzer in a nitrogen atmosphere at a heating rate of 20 $^{o}$C/min from 20 to 800 $^{o}$C. Differential scanning calorimetry (DSC) was carried out on a Shimadzu DSC-60Plus instrument with heating and cooling the system twice between temperatures of 30 and 300 $^{o}$C under a nitrogen atmosphere. Cyclic voltammetry (CV) was carried out by the Versastat II electrochemical work station at a scan rate of 100 mV/s, using a platinum carbon electrode as the working electrode, a platinum wire as the counter electrode, a saturated calomel electrode as the reference electrode and 0.1 M $TBAPF_6$ as electrolyte.

## Devices Fabrication and Testing

First of all, the glass substrates precoated with indium tin oxide (ITO) were cleaned by ultrasonic with deionized water, absolute ethanol and acetone successively, and then treated with UV-ozone for 15 min to completely remove the organic matter adsorbed on the surface and improve the surface hydrophilicity. Then, PEDOT: PSS solution filtered by 0.22 μm filter was spin-coated onto ITO at 3500 r/min for 50 s. After baking at 140 °C for 20 min, the coated substrates were transferred to a glove box under a nitrogen environment, and then different HTMs (in chlorobenzene solution of 10 mg/mL) were spun at 1500 r/min and heated at 120 °C for 15 min. Then again the as-prepared green perovskite QDs dissolved in n-octane were spin-coated at 2000 r/min

and baked at 60 °C for 10 min. The film thickness was measured via a full spectrum ellipsometer (SE950-D, Zhidong Optoelectronics), which is determined by using the reflection of polarized light on the upper and lower surfaces of the film to obtain the relationship between optical parameters and polarization state through Fresnel formula and Snell's law. The expected film thickness (a margin of error of 1 nm) was obtained by multiple spin-coating. Finally, the substrates were transferred to the vaporizer under a high vacuum of $4\times10^{-4}$ pa and TPBi (40 nm)/LiF (1.5 nm)/Al (100 nm) were thermally deposited in sequence. The device emission area was 9 $mm^2$ as determined by the overlapping zones between ITO anode and Al cathode.

The *EQE*, current density-voltage-luminance curves and electroluminescence (EL) spectra were measured through an integrated LED test system including fiber integrated field, Keithley 2400 source and PMA-12 spectrometer, which was designed by Hamamatsu Photonics Co., Ltd.. Moreover, all the tests were carried out in a glove box filled with nitrogen at room temperature.

## Experimental Section

**Synthesis.** All reagents and solvents used as from commercial sources without further purification.

**2-(4-chlorophenyl)-9,9'-spirobi[fluorene] (1)**

Compound **1** was synthesized by Suzuki coupling reaction. The mixture of 2-bromo-9,9'-spirobi[fluorene] (10.00 g, 25.29 mmol), (4-chlorophenyl)boronic acid (5.93 g, 37.92 mmol), $K_2CO_3$ (7.00 g, 50.58 mmol) and $Pd(PPh_3)_2Cl_2$ (0.3 g, 3 wt%) were dispersed in Toluene (60 mL), ethanol (30 mL) and water (30 mL). The reaction mixture was magnetically stirred at 76 $^oC$ for 5 hours under $N_2$ and then allowed to cool to room temperature. Water was removed by separatory funnel and the organic layer was filtered with silica gel column. The filter liquor was concentrated to 10 mL and white product was precipitated after addition of ethanol (20 mL). The ulteriorly extracted by filtration and the filter cake was washed by ethanol, 9.36 g dried product

was gained, yield of 89%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 3H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.43 - 7.35 (m, 5H), 7.30 (d, *J* = 2.0 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 3H), 6.92 (d, *J* = 1.3 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 7.6 Hz, 1H).

**2,2',7-tribromo-7'-(4-chlorophenyl)-9,9'-spirobi[fluorene] (2)**

Intermediate **2** was synthesized according to literature method.[1] Compound **1** (9.00 g, 21.08 mmol) was dissolved in DCE (90 mL) in a Singleneck round-bottom flask. 3 granules of $I_2$ were added followed by the mixed solution of dibromine (11.12 g, 69.56 mmol) and DCE (20 mL) drop by drop. The reaction was refluxed for 20 h and then cooled to room temperature. The aqueous solution with sodium hydroxide and sodium sulfite was added dropwise to the reaction mixture and white solid was precipitated simultaneously. The product was obtained following filtered, washed, recrystallized and dried, 11.5 g, yield of 82%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 15.0, 8.1 Hz, 3H), 7.64 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.37 (d, *J* = 9.6 Hz, 3H), 7.32 (dd, *J* = 4.9, 3.5 Hz, 3H), 6.87 (dd, *J* = 14.1, 1.4 Hz, 3H).

**7'-(4-chlorophenyl)-*N*$^2$,*N*$^2$,*N*$^{2'}$,*N*$^{2'}$,*N*$^7$,*N*$^7$-hexakis(4-methoxyphenyl)-9,9'-spirobi[fluorene]-2,2',7-triamine (3)**

Sodium tert-butoxide (7.20 g, 76.54 mmol) was dispersed in Toluene (100 mL) in a threeneck round-bottom flask equipped with a magnetic stir bar and reflux condenser. The reaction was heated to reflux for 1 h. After cooled to room temperature, compound **2** (10.00 g, 15.07 mmol), bis(4-methoxyphenyl)amine (12.09 g, 52.74 mmol), $Pd_2(dba)_3$ (0.5 g, 5 wt%) and P(t-Bu)$_3$ (11 g, purity 10%) were added and the reaction refluxed for an additional 2 h. The solution was cooled to room temperature and concentrated by rotary evaporation. The residue was purified by column chromatography (eluent: petroleum ether/DCM = 3/1) to obtain the pure product as yellow powder, 10.56 g, yield of 63%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.46 (dd, *J* = 15.3, 8.1 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 4H), 7.31 (dd, *J* = 18.2, 8.2 Hz, 7H), 6.93 (d, *J* = 9.0 Hz,

9H), 6.84 (d, *J* = 7.9 Hz, 3H), 6.78 (d, *J* = 8.8 Hz, 9H), 6.61 (s, 2H), 3.78 (s, 18H). HRMS (ESI, *m/z*): $[M+H]^+$ calculated for $C_{73}H_{58}ClN_3O_6$, 1108.4092, found 1108.4084.

**$N^2$,$N^2$,$N^{2'}$,$N^{2'}$,$N^7$,$N^7$-hexakis(4-methoxyphenyl)-7'-(4'-(2-phenyl-1*H*-benzo[d]imidazol-1-yl)-[1,1'-biphenyl]-4-yl)-9,9'-spirobi[fluorene]-2,2',7-triamine (HT1)**

(4-(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)phenyl)boronic acid (0.63 g, 2.03 mmol), compound **3** (1.50 g, 1.35 mmol), $K_2CO_3$ (0.56 g, 4.06 mmol), $Pd(OAc)_2$ (0.03 g, 2wt%) and X-phos (0.06 g, 4wt%) in a solution of 6:3:3 Toluene/ethanol/water (20 mL) heated to reflux for 2 h under $N_2$. The solution was cooled to room temperature and concentrated by rotary evaporation. The crude product was then purified by column chromatography using petroleum ether/DCM (4/1, v/v) as the eluent to give a light yellow-green solid, 0.8 g, yield of 45%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.66 - 7.59 (m, 7H), 7.55 (t, *J* = 8.4 Hz, 5H), 7.51- 7.40 (m, 5H), 7.34 (d, *J* = 8.5 Hz, 5H), 7.31 - 7.27 (m, 5H), 6.96 (s, 2H), 6.87 (d, *J* = 9.0 Hz, 7H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 7H), 6.56 (d, *J* = 1.7 Hz, 2H), 3.75 - 3.64 (m, 18H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 155.35 (s), 152.12 (s), 150.16 (d, *J* = 96.8 Hz), 148.36 (s), 141.41 (s), 141.09 (s), 138.58 (s), 138.08 (s), 136.95 (s), 135.75 (s), 134.91 (s), 129.73 (d, *J* = 34.0 Hz), 128.51 (s), 128.29 (s), 127.71 (s), 127.53 (s), 127.35 (s), 126.51 (s), 125.33 (s), 123.72 (s), 123.43 (s), 122.60 (s), 122.11 (s), 120.80 (s), 119.63 (s), 117.77 (d, *J* = 4.0 Hz), 114.54 (s), 110.69 (s), 77.27 (s), 77.05 (s), 76.84 (s), 55.49 (d, *J* = 6.9 Hz). HRMS (ESI, *m/z*): $[M+H]^+$ calculated for $C_{73}H_{58}ClN_3O_6$, 1342.5483, found 1342.5475.

**$N^2$,$N^2$,$N^{2'}$,$N^{2'}$,$N^7$,$N^7$-hexakis(4-methoxyphenyl)-7'-(4'-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-9,9'-spirobi[fluorene]-2,2',7-triamine (HT2)**

Reaction and purification conditions were the same as for **HT1**, except (4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)boronic acid (0.64 g, 2.03 mmol) was used.

Light yellow-green solid was finally obtained, 1.2 g, yield of 67%.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 4H), 7.55 - 7.51 (m, 8H), 7.48 (dd, *J* = 7.2, 3.7 Hz, 9H), 7.42 (d, *J* = 8.3 Hz, 3H), 7.32 (d, *J* = 6.3 Hz, 5H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.93 (d, *J* = 2.7 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 7H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 7H), 6.55 (s, 2H), 3.71 (s, 18H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 155.31 (s), 151.82 (s), 150.41 (s), 149.84 (s), 148.33 (s), 141.79 (s), 141.42 (s), 140.93 (d, *J* = 11.9 Hz), 138.71 (s), 138.52 (s), 137.15 (s), 136.86 (s), 134.99 (s), 130.00 (d, *J* = 19.4 Hz), 128.86 (s), 127.63-127.15 (m), 126.80 (s), 126.49 (s), 125.30 (s), 123.49 (d, *J* = 43.1 Hz), 122.61 (s), 122.09 (s), 120.76 (s), 119.58 (s), 117.80 (s), 114.53 (s), 110.56 (s), 77.26 (s), 77.05 (s), 76.84 (s), 55.49 (d, *J* = 6.7 Hz). HRMS (ESI, *m/z*): $[M+H]^+$ calculated for $C_{73}H_{58}ClN_3O_6$, 1342.5483, found 1342.5481.

## Additional Data

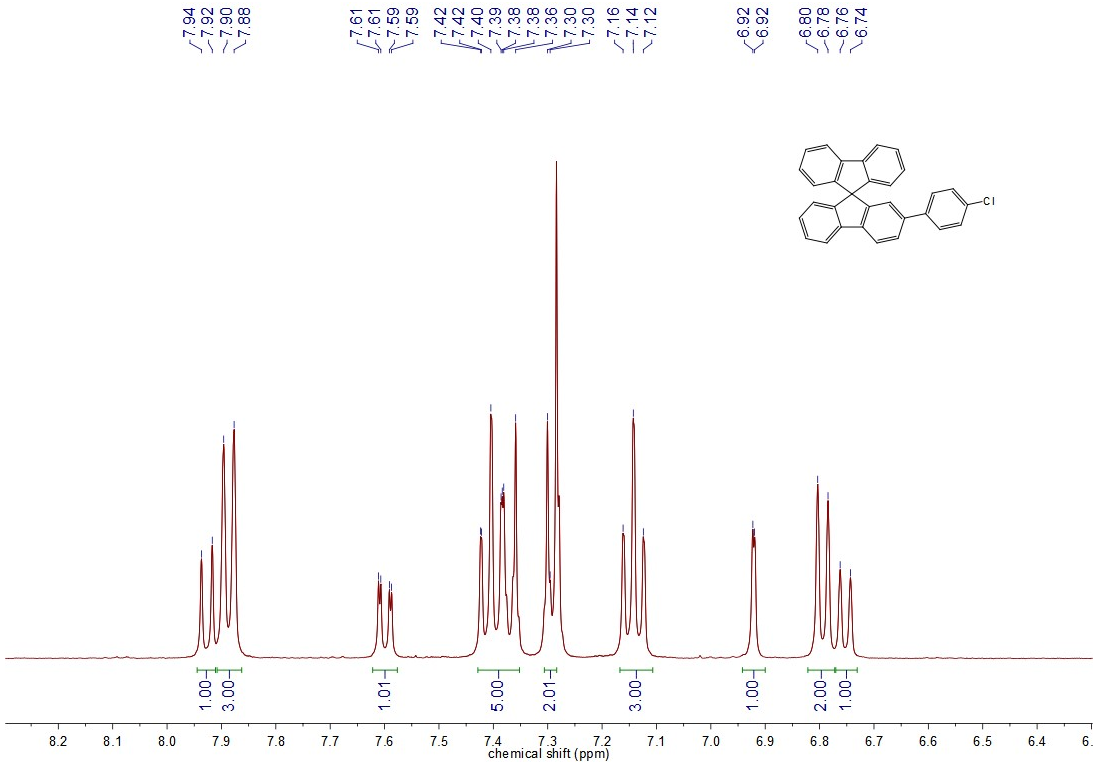



**Fig. S1** $^{1}$H NMR spectrum of Compound **1**.

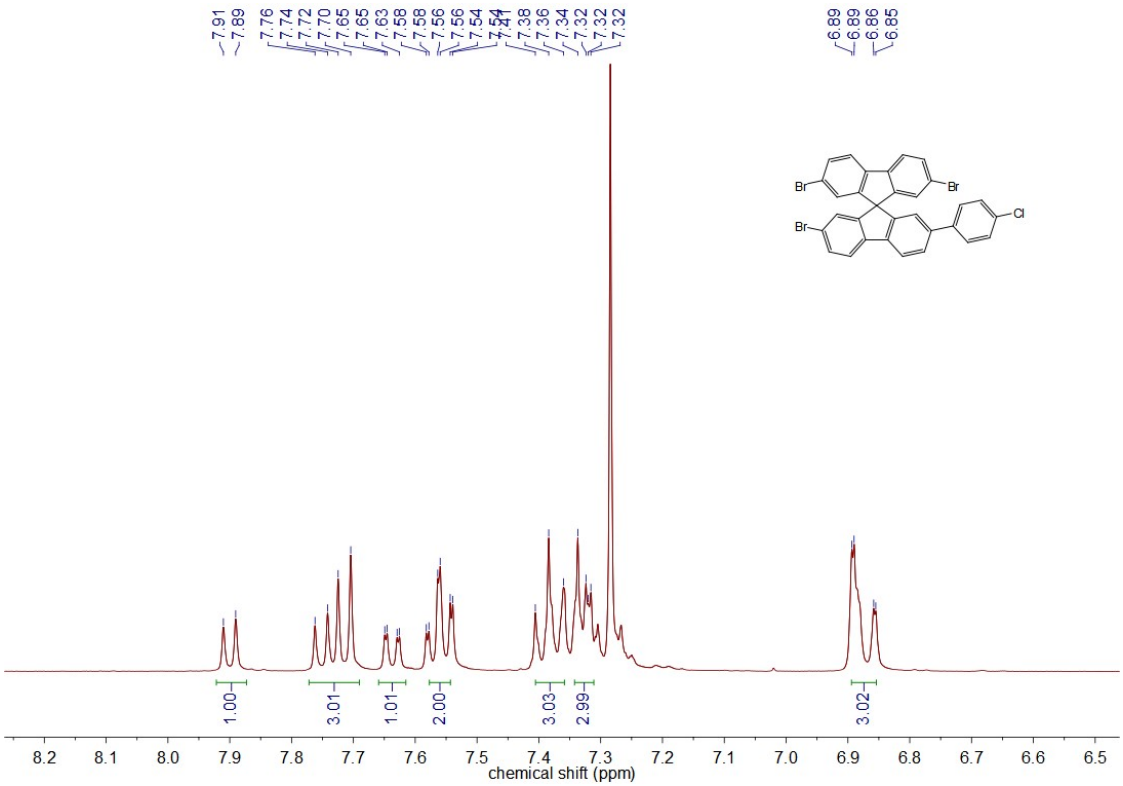



**Fig. S2** $^{1}$H NMR spectrum of Compound **2**.

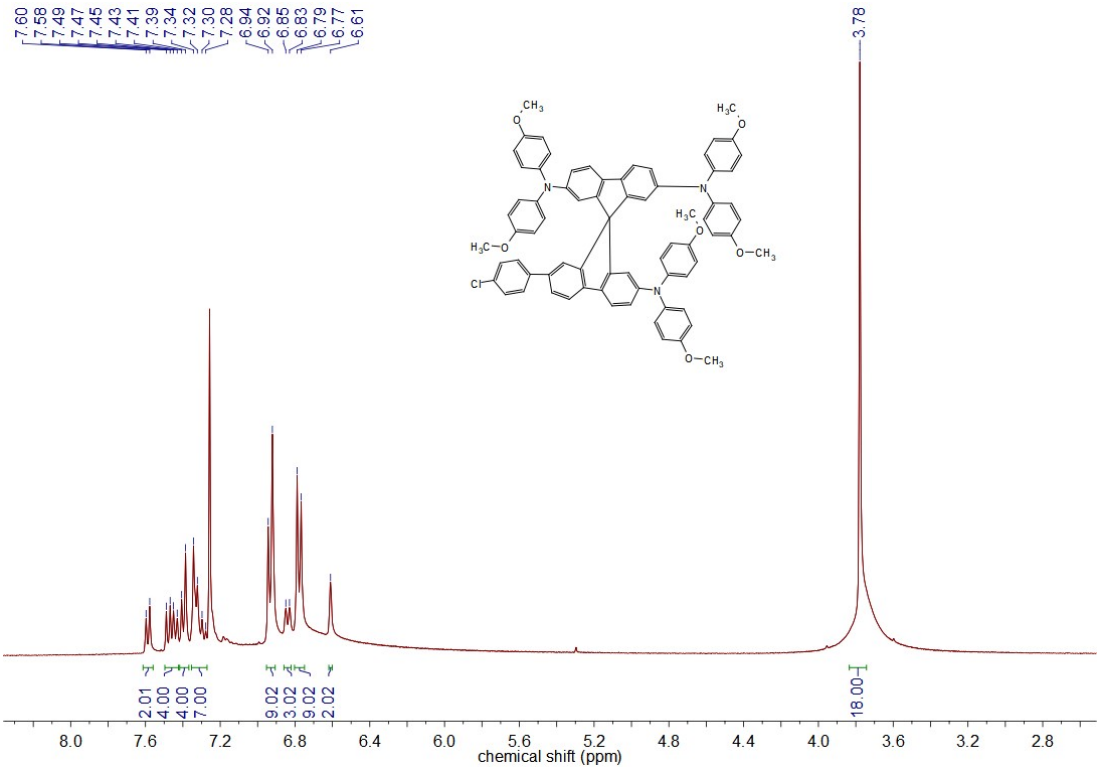



**Fig. S3** $^{1}$H NMR spectrum of Compound **3**.

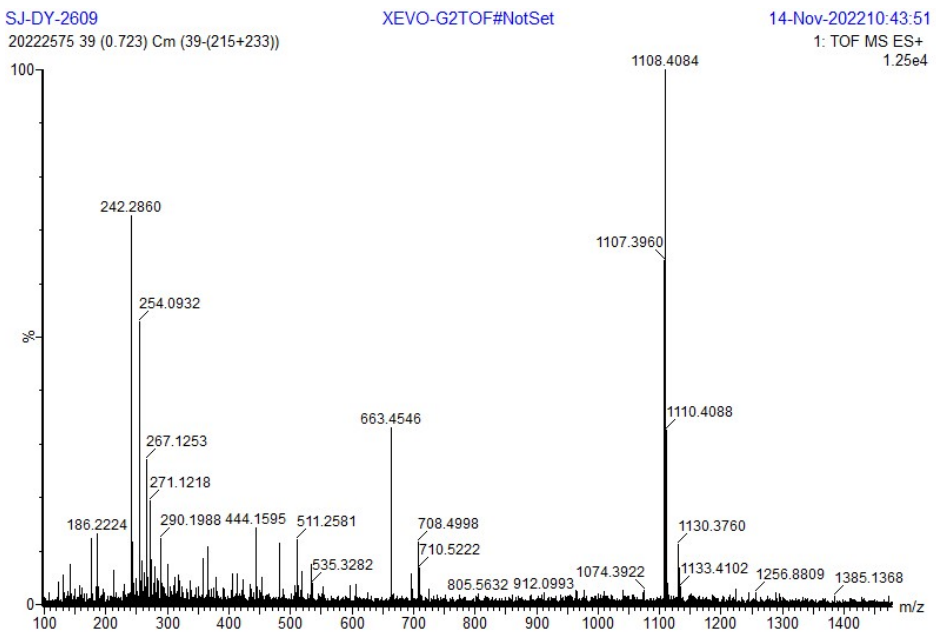
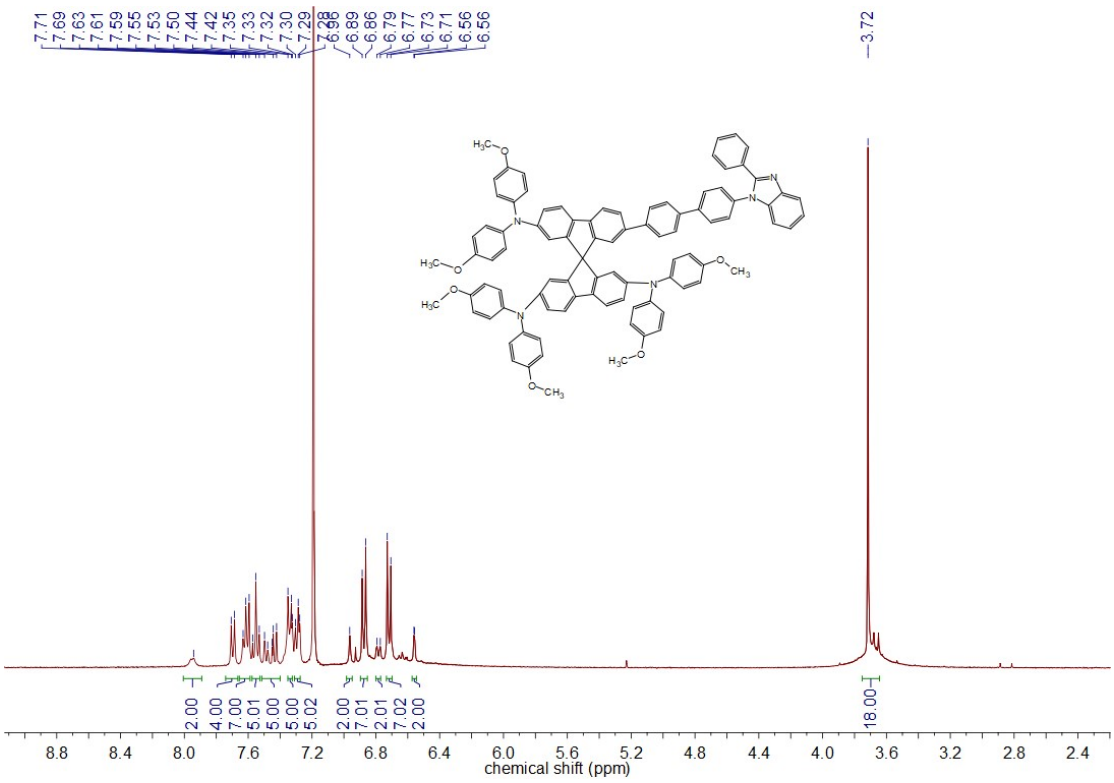



**Fig. S4** The MS of Compound **3**.



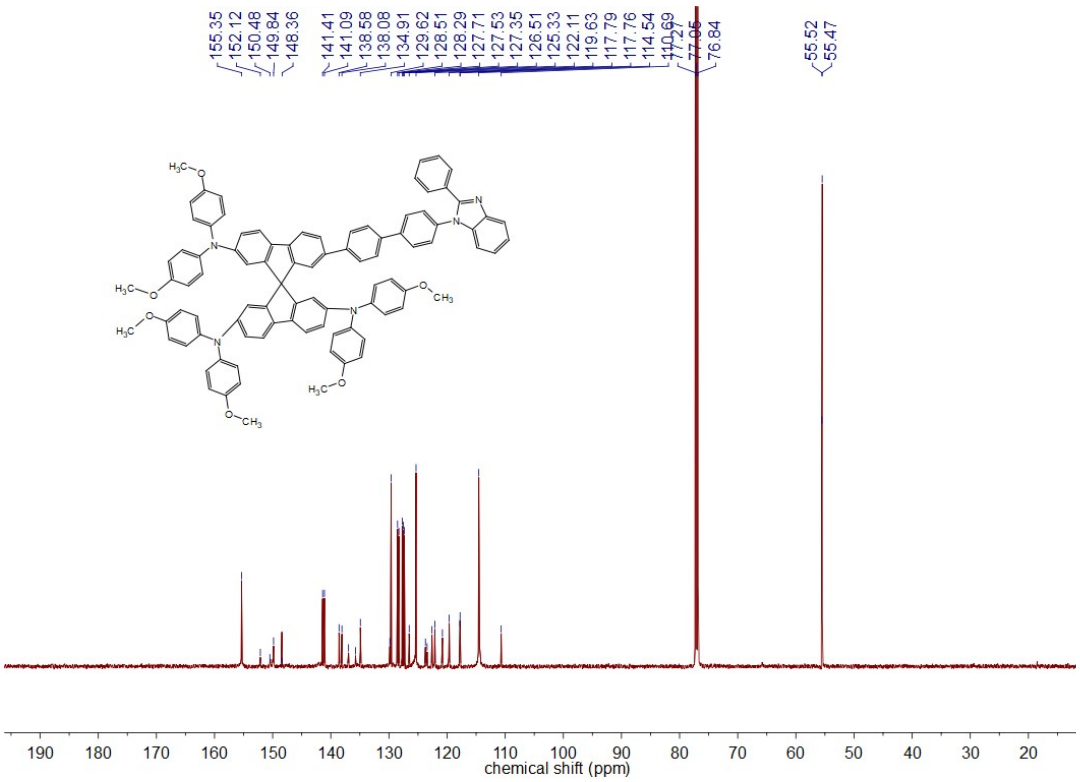



**Fig. S5** $^{1}$H NMR spectrum and $^{13}$C NMR spectrum of **HT1**.

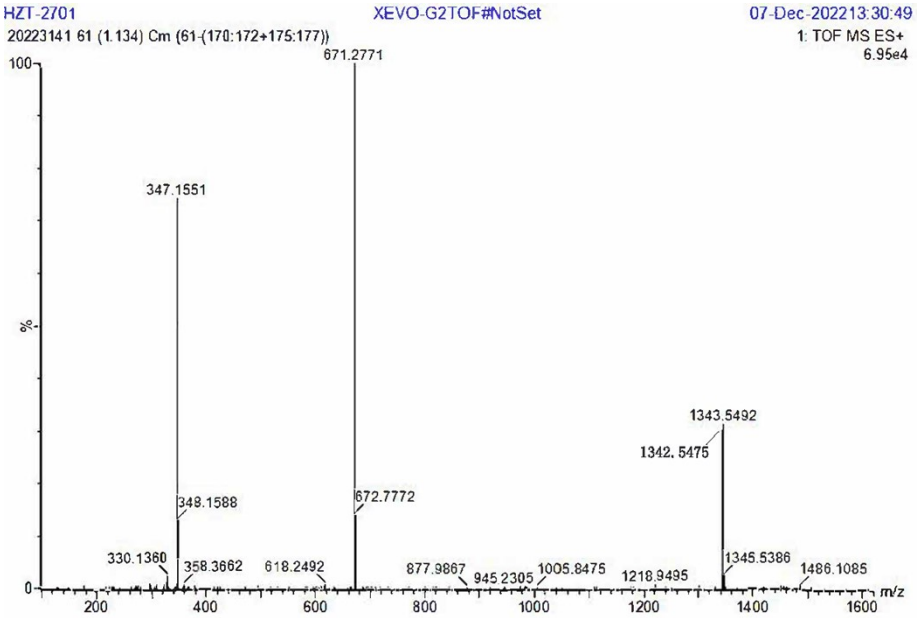



**Fig. S6** The MS of **HT1**.

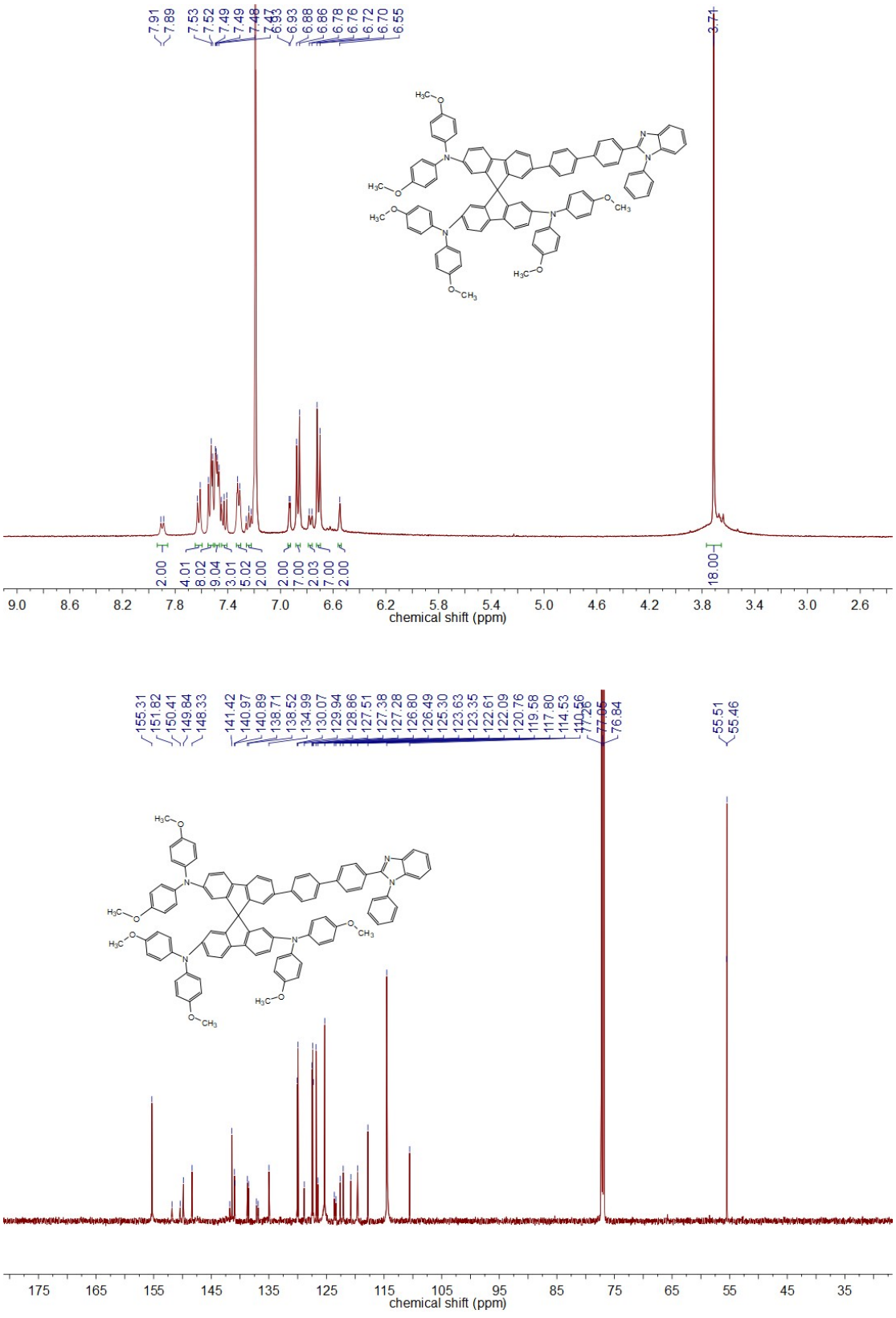



**Fig. S7** $^{1}$H NMR spectrum and $^{13}$C NMR spectrum of **HT2**.

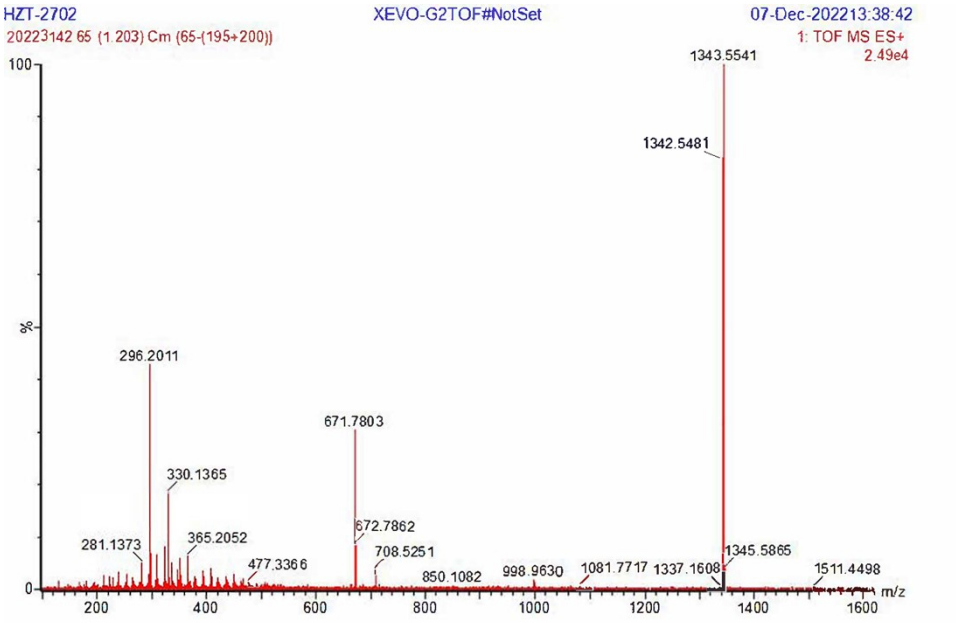



**Fig. S8** The MS of **HT2**.

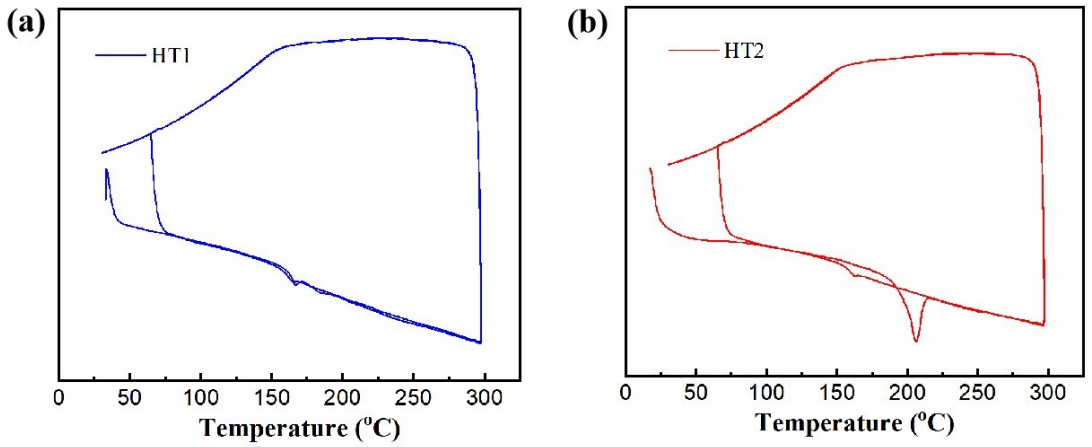



**Fig. S9** The DSC curves of the HTMs **HT1** (a) and **HT2** (b) for full heating scans.

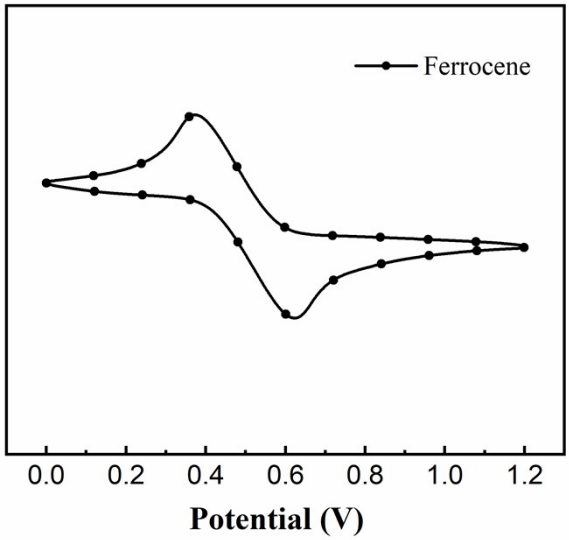



**Fig. S10** Cyclic voltammetry of ferrocene in $CH_2Cl_2$.

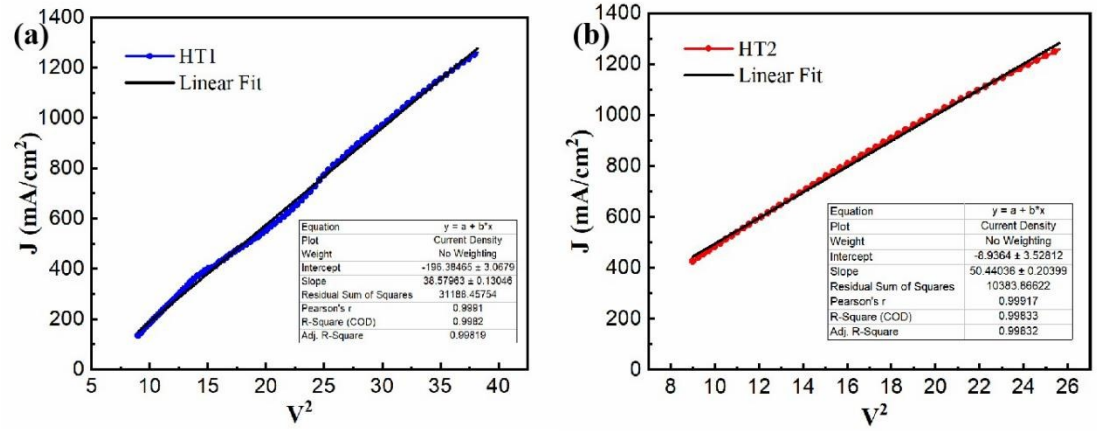



**Fig. S11** The linear fitting results of the *J-V* curves for the device based on **HT1** (a) and **HT2** (b).

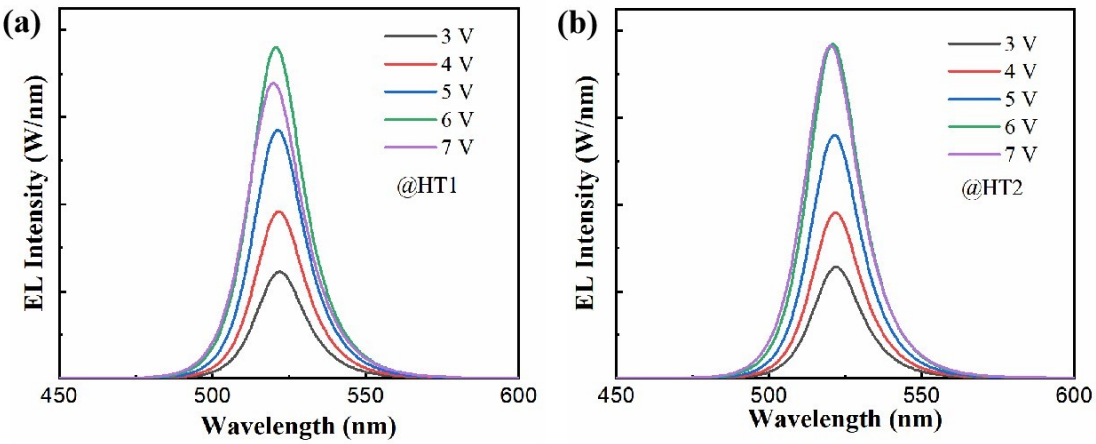


**Fig. S12** EL spectra of green Pe-QLEDs in the range of 3-7 V.

**Table S1.** Summary of EL performance of reported green Pe-QLEDs recently.

| HTMs | $L_{max}$ [cd/m$^2$] | $EQE_{max}$ [%] | $_{c,max}$ [cd/A] | Year | Reference |
|---|---|---|---|---|---|
| poly-TPD | 15185 | 6.27 | 13.3 | 2017 | Ref. 1 |
| TFB | 46000 | 5.7 | 19.9 | 2018 | Ref. 2 |
| TFB/TOPO | 3907 | 6.7 | 18.8 | 2020 | Ref. 3 |
| PEDOT:PSS | 18154 | 9.6 | / | 2020 | Ref. 4 |
| PEDOT:PSS/AT | 11000 | 14.7 | 45.4 | 2022 | Ref. 5 |
| EA-PEDOT:PSS | 32500 | 9.6 | 30.3 | 2022 | Ref. 6 |
| **HT1** | 45056 | 7.6 | 29.4 | 2023 | This work |
| **HT2** | 46382 | 6.7 | 25.8 | 2023 | This work |

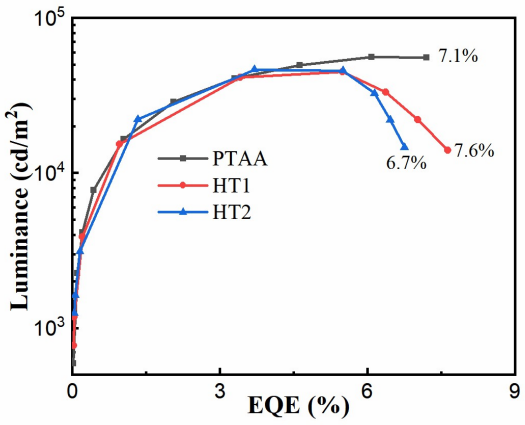



**Fig. S13** Luminance versus *EQE* (*L-EQE*) characteristics of the devices based on **HT1**, **HT2** and **PTAA** under the same operating conditions.

## Reference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