Supporting Information for:

The Synthesis of novel AIE Emitters with triphenylethene-carbazole skeleton and para-/meta- substituted arylboron groups and their application in efficient non-doped OLEDs

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1. Experimental Section

General information

All reagents were used as received from J&K and TCI without further purification unless otherwise stated. Solvents were freshly distilled according to the standard procedures. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX400 NMR spectrometer using chloroform-d as solvent and tetramethylsilane (TMS) as internal reference. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT TSQ 7000 Mass Spectrometer System operating in a MALDI-TOF mode. Elemental analyses were performed on an Element Analysis System. UV absorption spectra were taken on a Milton Ray Spectronic 3000 array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer spectrofluorometer LS 55. Cyclic voltammetry (CV) was performed on a CHI-600C electrochemical analyzer. The CV measurements were carried out with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and an Ag/AgCl reference electrode, and the scan speed was 50 mV/s. (TGA) was performed on a TGA 2050 thermogravimetric analyzer under an N_2 atmosphere with a heating rate of 10 °C /min from room temperature to 750 °C. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC differential scanning calorimeter under a N_2 atmosphere with a heating rate of 10 °C /min from room temperature to 250 °C.

Device fabrication

The multilayer OLEDs were fabricated by the vacuum-deposition method. Organic layers were deposited by high-vacuum (5×10^{-4} Pa) thermal evaporation onto a glass (3 cm×4 cm) substrate pre-coated with an indium tin oxide (ITO) layer. Dipyrazinoquinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) was used as the hole injection layer, N,N-bis(naphthalene)-N,N-bis(phenyl)benzidine (NPB) was used as the hole-transport layer (HTL), the synthesized compound was used as the emitting layer, 1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi) was used as the electron-transport layer (ETL) and LiF/Al was used as the cathode. All organic layers were deposited sequentially. Thermal deposition rates for the organic materials, LiF and Al were 0.5, 0.5 and 1 Å/Second, respectively. The active area of each device was 12 mm^2. The electroluminescent spectra were measured on a Hitachi MPF-4 spectrofluorometer. The current density-voltage (V-J) characteristics of the OLEDs were recorded on a Keithley 2400 Source Meter. The current density-voltage-luminance curves (B-I-V) characterizations were carried out with a 3645 DC power supply combined with a 1980A spot photometer and were recorded simultaneously. All measurements were done at room temperature under ambient conditions.

Theoretical calculations

The ground-state geometry of these molecules was optimized at the B3LYP level with the 6-31G(d, p) basis set. All calculations were carried out with the Gaussian 03 program package and performed at the Supercomputing Centre of the Computer Network Information Centre of the Chinese Academy of Sciences.

Synthesis and characterization

(4-bromophenyl)(9-ethyl-9H-carbazol-3-yl)methanone (1)

A stirred mixture of N-ethylcarbazole (1.953 g, 10 mmol) and 4-bromobenzoylchloride (1.410 g, 10 mmol) in 35 mL CH_2Cl_2 was treated by slow addition of aluminum chloride (1.330 g, 10 mmol) under an atmosphere of nitrogen. The mixture was heated at 40 °C for 24 h. After cooling to room temperature, cold water (200 mL) was added and the organic layer extracted with dichloromethane, washed with water, diluted hydr°Chloric acid, dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The crude product was purified by silica-gel chromatography (eluent) to give a white solid in 70% yield (2.65 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.57 (d, J = 1.86 Hz, 1H), 8.12-8.11 (d, J = 7.81 Hz, 1H), 8.01-7.99 (d, J = 6.77 Hz, 1H), 7.72 (s, 1H), 7.71 (s, 1H), 7.66 (s, 1H), 7.65 (s, 1H), 7.53 (t, J = 14.14 Hz, 1H), 7.47-7.45 (t, J = 15.01 Hz, 2H), 7.31-7.28 (t, J = 13.63 Hz, 1H), 4.44-4.40 (q, J = 21.15 Hz, 2H), 1.49-1.47 (t, J = 14.36 Hz, 3H).

3-[1-(4-bromophenyl)-2,2-diphenylvinyl]-9-ethyl-9H-carbazole (2)

Under a nitrogen atmosphere, n-butyllithium (2.4 M, 2.92 mL, 7.0 mmol) was added dropwise to a solution of diphenylmethane (1.20 mL, 7.0 mmol) in THF (40 mL) at 0 °C followed by stirring for 0.5 h. Then, the mixture was transferred to a solution of 1 (2.20 g, 5.82 mmol) in THF (50 mL) at 0 °C. The resulting mixture was stirred at room temperature for 24 h. The reaction was quenched by adding a saturated aqueous solution of ammonium chloride followed by extraction with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$. After filtration and solvent evaporation, the resulting crude product was dissolved in 80 mL toluene, into which a catalytic amount of p-toluenesulfonic acid (1.72 g, 10 mmol) was added. After heating to reflux for 18 h, the mixture was cooled to room temperature, washed with brine to remove the p-toluenesulfonic acid, and dried over anhydrous $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography to give a light yellow solid in 36% yield (1.10 g). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.87-7.86 (d, J = 7.89 Hz, 1H), 7.70 (s, 1H), 7.43-7.40 (d, J = 14.10 Hz, 1H), 7.36-7.35 (d, J = 8.13 Hz, 1H), 7.23 (t, J = 4.23 Hz, 1H), 7.22 (t, J = 4.14 Hz, 1H) 7.16-7.12 (m, 4H), 7.11 (s, 2H), 7.08-7.02 (m, 7H), 6.97 (t, J = 4.01 Hz, 1H), 6.96 (t, J = 4.07 Hz, 1H), 4.31-4.27 (q, J = 21.64 Hz, 2H), 1.41-1.39 (t, J = 14.27 Hz, 3H).

3-{1-[4-(dimesitylboryl)phenyl]-2,2-diphenylvinyl}-9-ethyl-9H-carbazole (p-DPDECZ)

A 100 mL round-bottom flask containing 2 (0.985 g, 1.865 mmol) was evacuated and flushed with dry nitrogen three times followed by the addition of dry THF (80 mL). The mixture was cooled to -78 °C and n-BuLi (2.4 M in hexane, 1.55 mL, 3.73 mmol) was added dropwise with a syringe. After stirring for 4 h at -78 °C, dimesitylboron fluoride (1.099 g, 4.103 mmol) was slowly added to the mixture, which was subsequently allowed to warm to room temperature, while stirring was continued for 24 h. The mixture was quenched with ice water (200 mL) and stirred for 2 h. The organic layer was extracted with CH_2Cl_2 and the combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography. DPDECZ was obtained as a yellow-green solid in 69.2% yield (0.90 g). ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83-7.82 (d, J = 7.67 Hz, 1H), 7.72 (s, 1H), 7.42-7.39 (t, J = 14.92 Hz, 1H), 7.35-7.34 (d, J = 8.20 Hz, 1H), 7.24 (s, 1H), 7.15-7.13 (m, J = 12.45 Hz, 2H), 7.11 (s, 1H), 7.10-7.09 (d, J = 4.94 Hz, 2H), 7.08-7.07 (t, J = 3.92 Hz, 3H), 7.06-7.05 (t, J = 4.73 Hz, 3H), 7.03-7.02 (d, J = 4.29 Hz, 5H), 6.78 (s, 4H), 4.30-4.26 (q, J = 21.34 Hz, 2H), 2.27 (s, 6H), 1.98 (s, 12H), 1.41-1.39 (t, J = 14.22 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 146.30, 145.07, 145.00, 144.89, 144.75, 144.31, 143.97, 142.34, 140.62, 138.96, 136.34, 133.57, 132.87, 132.76, 130.57, 130.04, 129.74, 128.52, 128.12, 126.85, 126.60, 126.40, 126.25, 126.10, 124.21, 123.86, 122.52, 120.60, 119.42, 109.15, 108.45, 43.85, 33.56, 31.25, 26.37, 21.85, 13.98. MS: (m/z) 697.3861, Anal. Calcd for $C_{52}H_{48}BN$: C 89.51%, H 6.93% and N 2.01%. Found: C 89.72%, H 7.00%, and N 1.96%.

3-{1-(4'-(dimesitylboryl)-[1,1'-biphenyl]-4-yl)-2,2-diphenylvinyl}-9-ethyl-9H-carbazole (p-DBPDECZ)

Into a 100 mL two-necked round-bottom flask was placed 2 (0.53 g, 1.0 mmol), (4-(dimesitylboryl)phenyl)boronic acid (0.55 g, 1.4 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and K_2CO_3

(552 mg, 4.0 mmol). The flask was evacuated under a vacuum and flushed with dry nitrogen three times, and then 50 mL of THF and 15 mL of water were added. The reaction mixture was refluxed for 24 h. After cooling to room temperature, the organic layer was extracted with CH_2Cl_2 and the combined organic extracts were dried over anhydrous MgSO4. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography. Yellow solid of DBDECZ was isolated in 70% yield. (0.53g) ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.90-7.89 (d, J = 7.90 Hz, 1H), 7.78 (s, 1H), 7.60-7.56 (q, J = 20.33 Hz, 4H), 7.47-7.39 (m, 4H), 7.21-7.06 (m, 15H), 6.85 (s, 4H), 4.34-4.30 (q, J = 21.34 Hz, 2H), 2.34 (s, 6H), 2.05 (s, 12H), 1.44-1.42 (t, J = 13.89 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 140.84, 138.58, 137.06, 132.14, 131.54, 129.69, 128.17, 127.79, 127.66, 126.30, 126.26, 126.22, 126.16, 125.49, 123.53, 123.00, 122.50, 120.43, 118.75, 108.44, 107.54, 37.58, 23.48, 21.24, 13.87. MS: (m/z) 773.4252, Anal. Calcd for $C_{58}H_{52}BN$: C 90.02%, H 6.77% and N 1.81%. Found: C 89.99%, H 6.80%, and N 1.81%.

(3-bromophenyl)(9-ethyl-9H-carbazol-3-yl)methanone (3)

Synthesis of 3 was similar to that of 1. White solid in 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.59 (d, J = 1.29 Hz, 1H), 8.13-8.11 (d, J = 7.82 Hz, 1H), 8.00-7.99 (d, J = 9.77 Hz, 1H), 7.97 (s, 1H), 7.75-7.72 (m, J = 21.54 Hz, 2H), 7.54-7.52 (t, J = 14.25 Hz, 1H), 7.47-7.45 (q, J = 13.93 Hz, 2H), 7.40-7.37 (t, J = 15.00 Hz, 1H), 7.31-7.28 (t, J = 14.90 Hz, 1H), 4.44-4.40 (q, J = 21.86 Hz, 2H), 1.49-1.47 (t, J = 14.25 Hz, 3H).

3-(1-(3-bromophenyl)-2,2-diphenylvinyl)-9-ethyl-9H-carbazole (4)

Synthesis of 4 was similar to that of 2. Light yellow solid in 35% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.91-7.90 (d, J = 7.81 Hz, 1H), 7.75 (s, 1H), 7.46-7.44 (t, J = 15.44 Hz, 1H), 7.40-7.39 (d, J = 7.63 Hz, 1H), 7.28-7.27 (d, J = 4.16 Hz, 2H), 7.20-7.06 (m, 14H), 7.00 (t, J = 15.27 Hz, 1H), 4.34-4.31 (q, J = 21.17 Hz, 2H), 1.45-1.43 (t, J = 14.23 Hz, 3H).

3-{1-(3-(dimesitylboryl)phenyl)-2,2-diphenylvinyl}-9-ethyl-9H-carbazole (m-DPDECZ)

Synthesis of m-DPDECZ was similar to that of p-DPDECZ. Green solid with 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82-7.81 (d, J = 7.99 Hz, 1H), 7.68 (s, 1H), 7.45-7.43 (t, J = 13.86 Hz, 1H), 7.39-7.37 (d, J = 8.14 Hz, 1H), 7.28 (d, J = 3.75 Hz, 1H), 7.23-7.22 (m, J = 11.64 Hz, 2H), 7.18-7.11

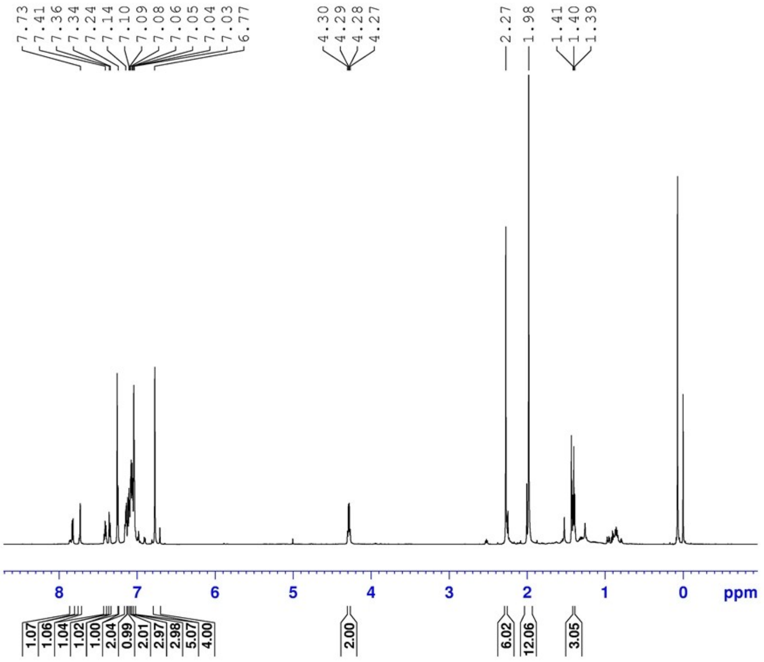
(m, 4H), 7.08-7.01 (m, 10H), 6.74 (s, 4H), 4.33-4.30 (q, J = 21.60 Hz, 2H), 2.27 (s, 6H), 1.90 (s, 12H), 1.44-1.42 (t, J = 14.40 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 141.81, 141.69, 140.76, 140.18, 139.72, 138.71, 138.59, 138.40, 134.84, 134.19, 133.77, 131.51, 131.43, 129.47, 128.01, 127.61, 127.52, 126.11, 126.02, 125.44, 123.38, 123.05, 122.38, 120.20, 118.72, 108.43, 107.43, 37.57, 29.74, 23.38, 21.21, 13.85. MS: (m/z) 697.3880, Anal. Calcd for $C_{52}H_{48}BN$: C 89.51%, H 6.93% and N 2.01%. Found: C 89.72%, H 7.00%, and N 1.96%.

3-{1-(4'-(dimesitylboryl)-[1,1'-biphenyl]-3-yl)-2,2-diphenylvinyl}-9-ethyl-9H-carbazole (m-DBPDECZ)

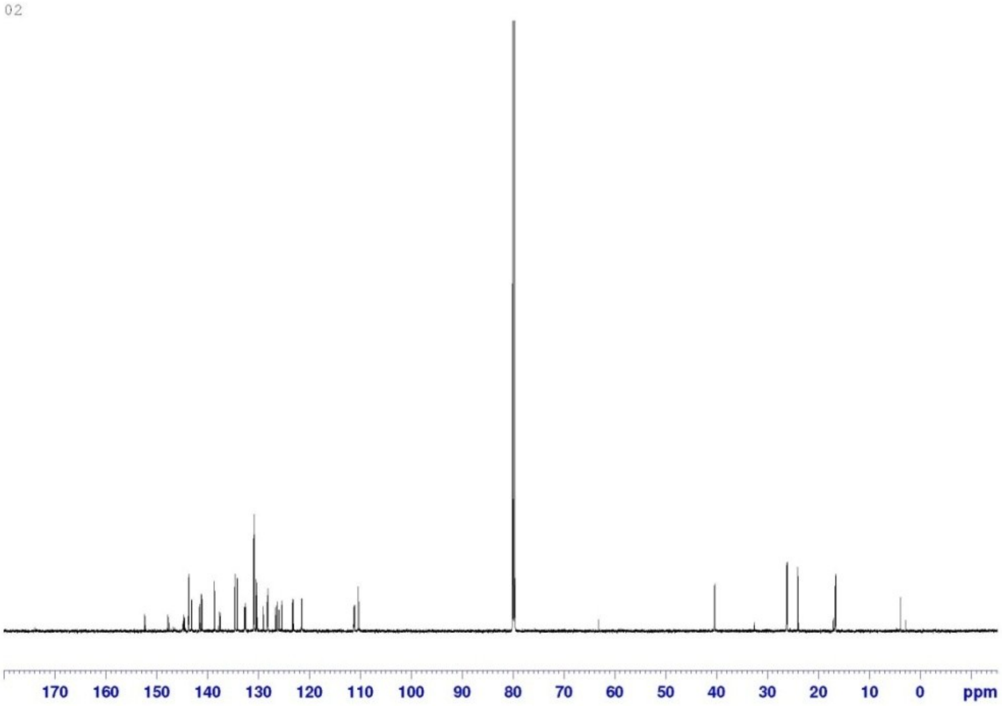
Synthesis of m-DBPDECZ was similar to that of p-DBPDECZ. White solid with 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.90-7.89 (d, J = 8.09 Hz, 1H), 7.81 (s, 1H), 7.60-7.38 (m, 6H), 7.34-7.05 (m, 17H), 6.85 (s, 4H), 4.33-4.30 (q, J = 19.64 Hz, 2H), 2.04 (s, 6H), 2.05 (s, 12H), 1.45-1.43 (t, J = 15.02 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 144.22, 141.81, 141.56, 140.84, 140.44, 139.85, 138.82, 138.57, 136.88, 134.32, 131.52, 131.05, 129.70, 128.15, 127.85, 127.68, 126.60, 126.39, 126.19, 125.50, 123.53, 123.02, 122.49, 120.43, 118.73, 108.45, 107.56, 37.59, 29.74, 23.50, 21.24, 13.89. MS: (m/z) 773.4202, Anal. Calcd for $C_{58}H_{42}BN$: C 90.02%, H 6.77% and N 1.81%. Found: C 90.00%, H 6.80%, and N 1.80%.

2. Results and Disccusion

2.1 Structure Characterization



^{1}H NMR spectra of p-DPDECZ in $CDCl_3$



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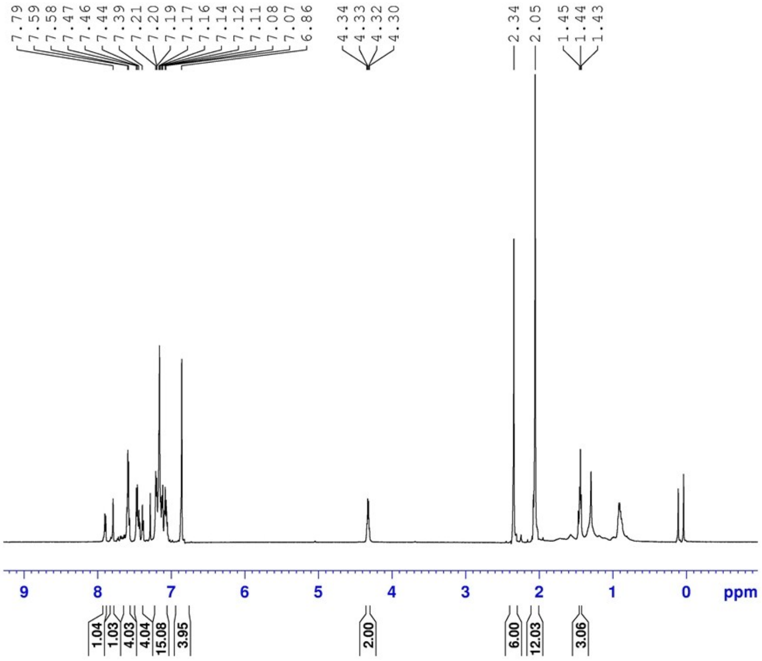

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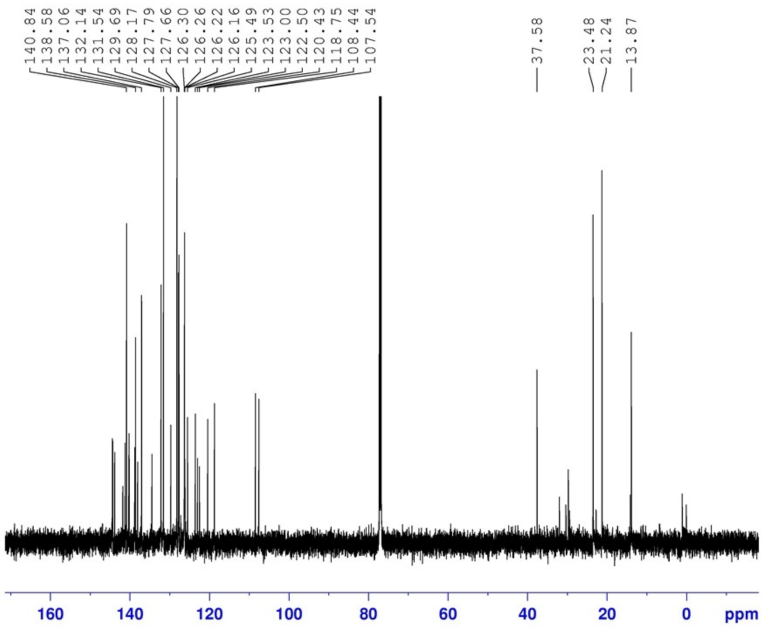

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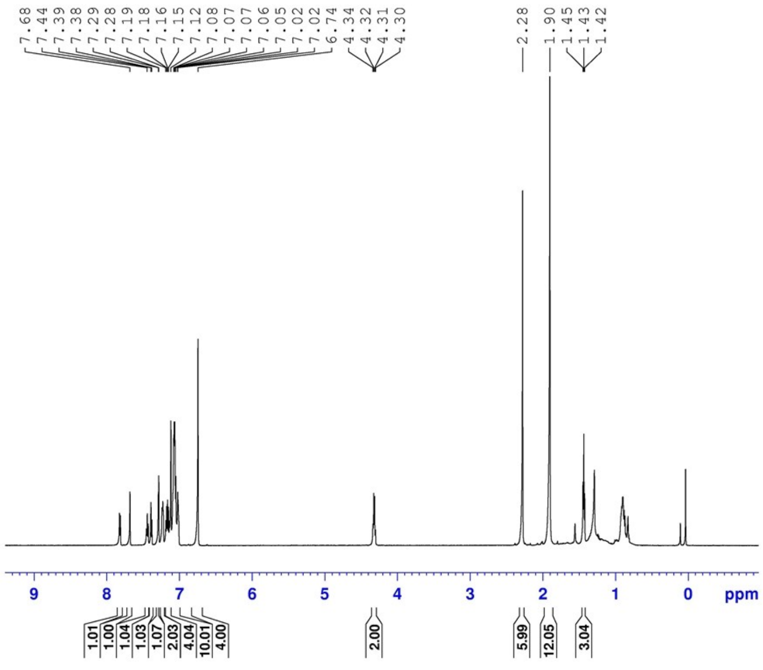

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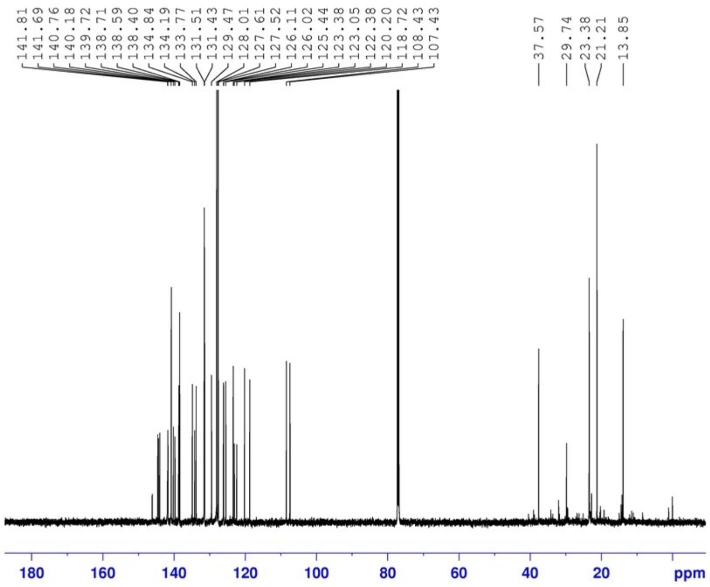

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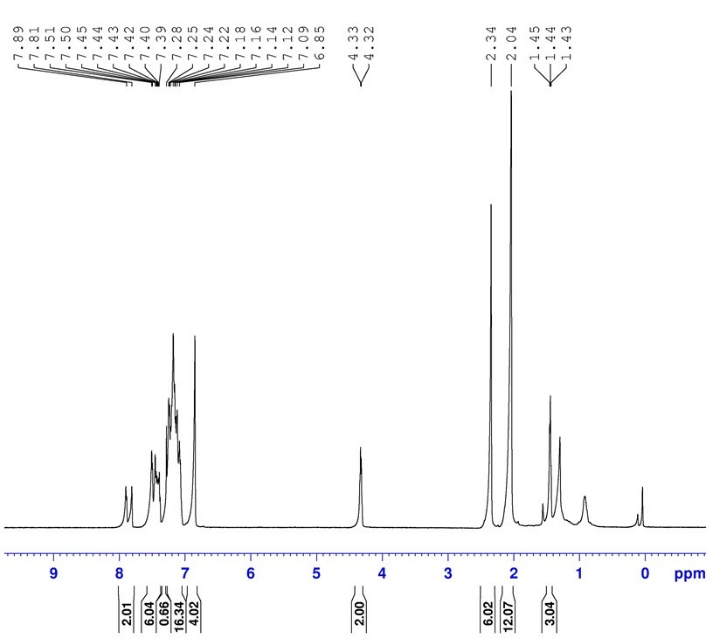

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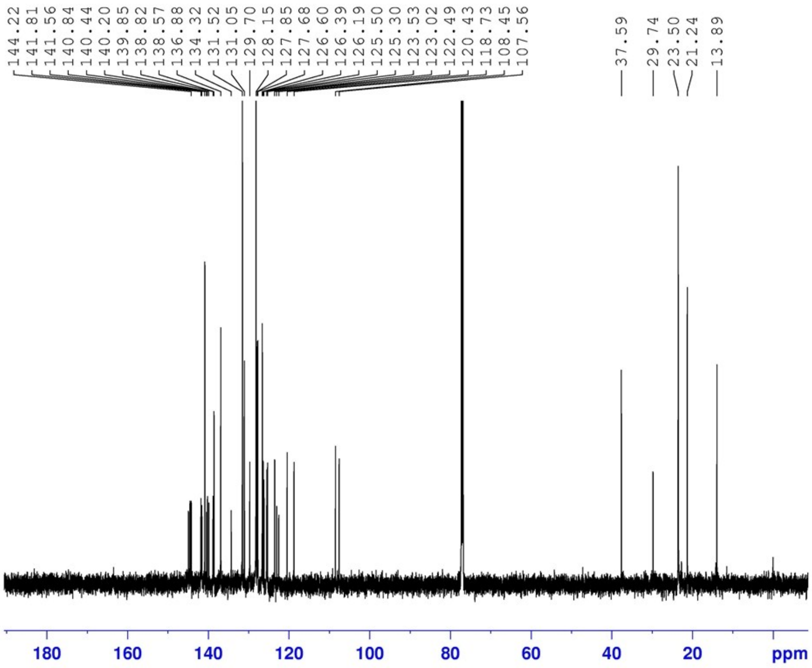

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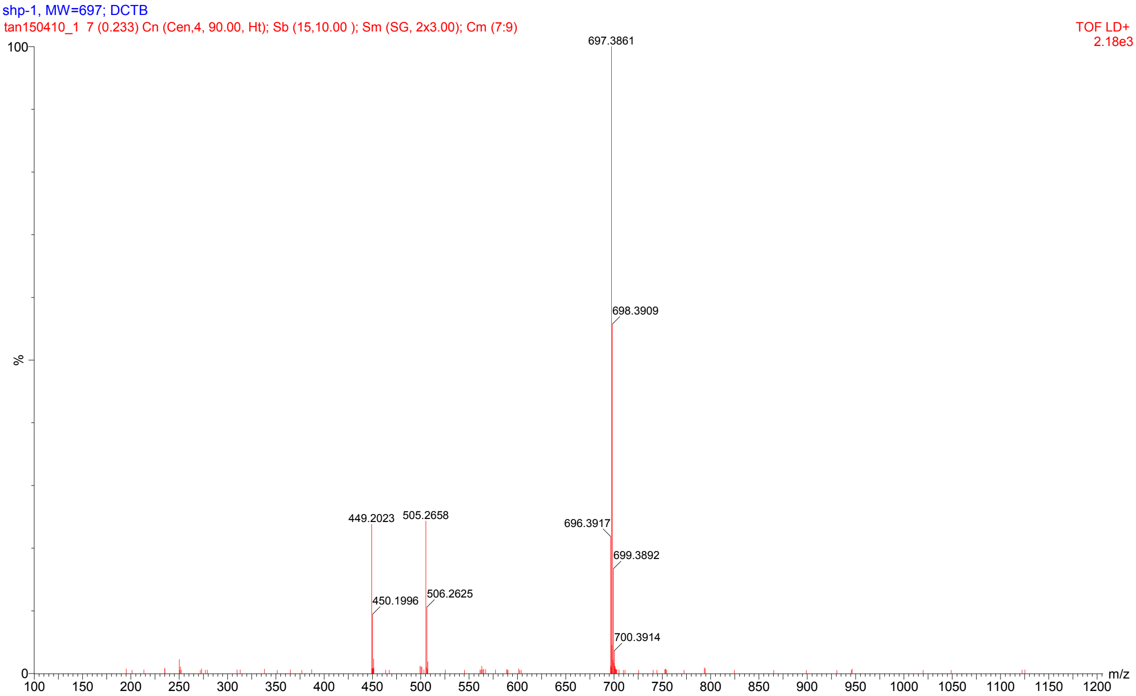
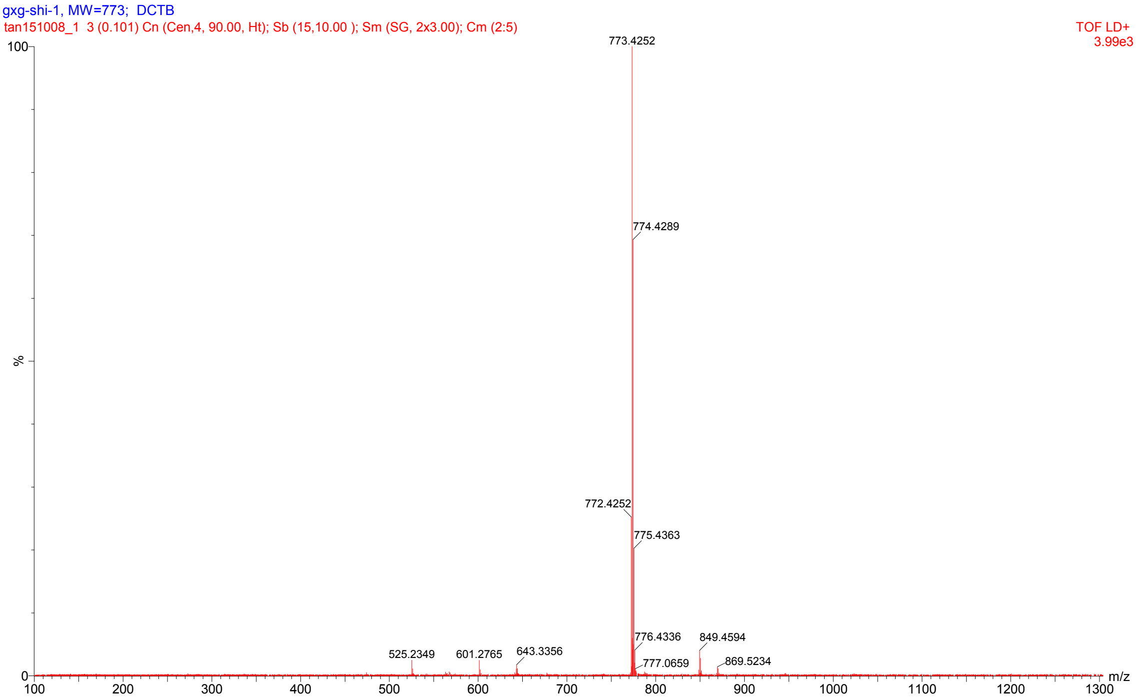
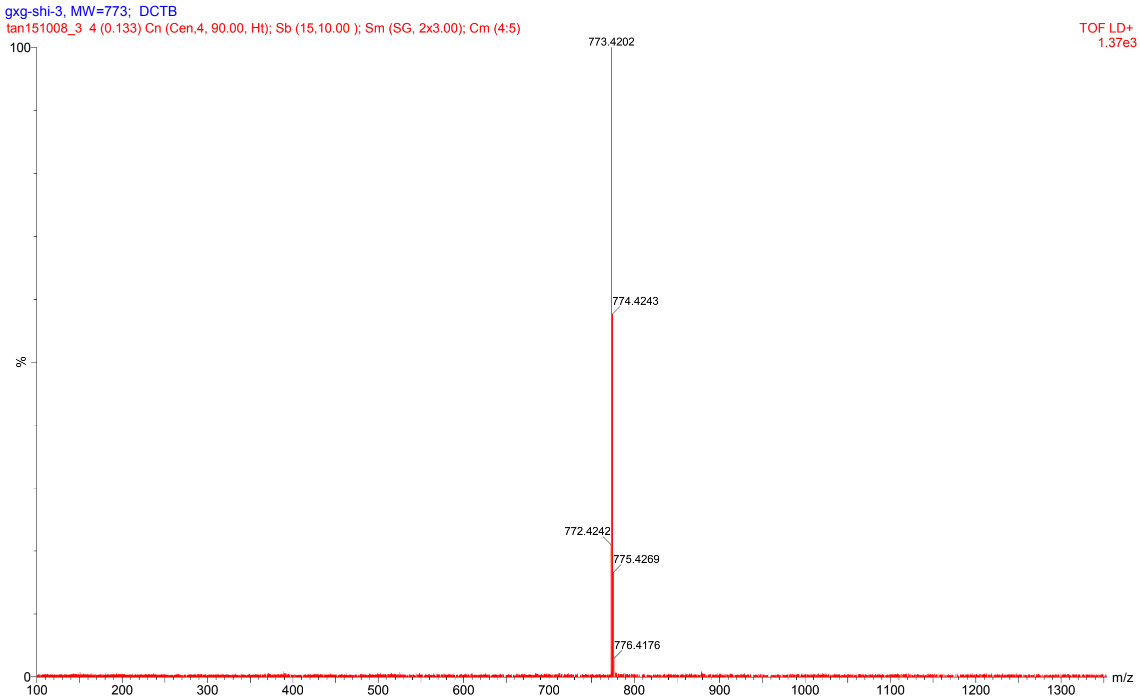


HRMS spectra of p-DPDECZ



HRMS spectra of p-DBPDECZ

HRMS spectra of m-DPDECZ



HRMS spectra of m-DBPDECZ

2.2 Thermal Properties

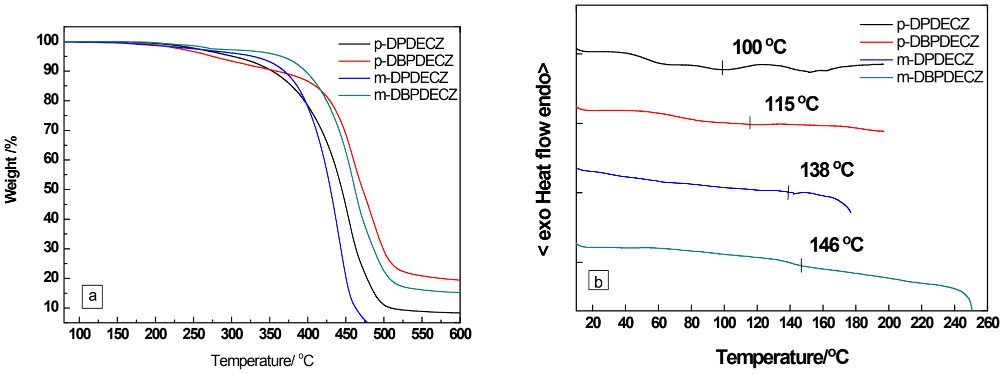


Figure S1. TGA curve (a) and DSC curve (b) of these AIE luminogens

2.3 Photophysical Properties

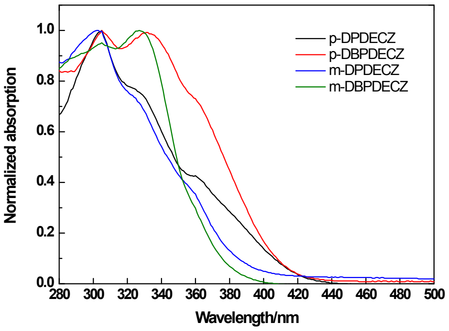


Figure S2. Normalized absorption spectra of these AIE luminogens in THF solution with a concentration of 10 μM

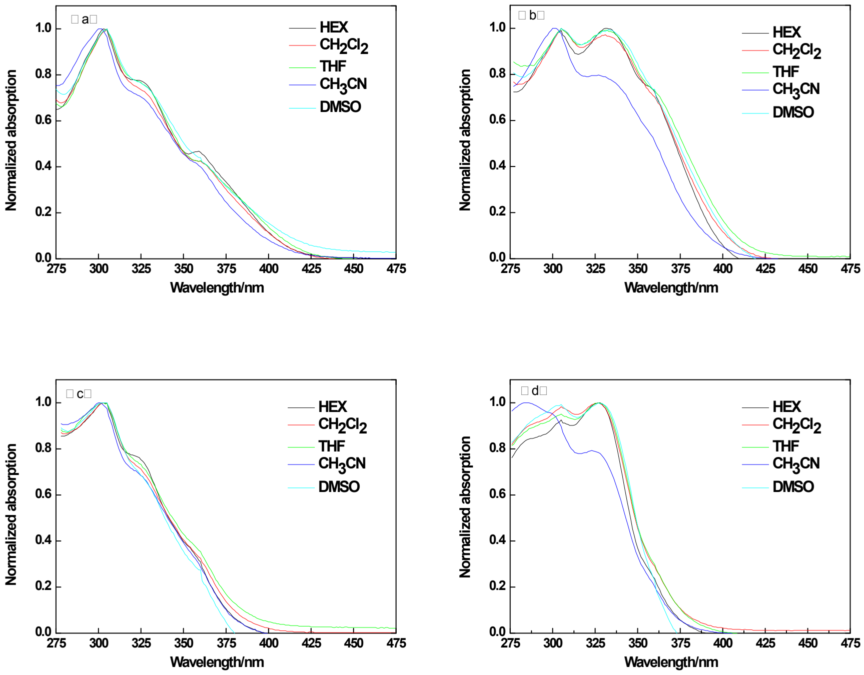


Figure S3. Normalized absorption spectra of p-DPDECZ (a), p-DBPDECZ (b), m-DPDECZ (c) and m-DBPDECZ (d) in various solutions with a concentration of 10 μM

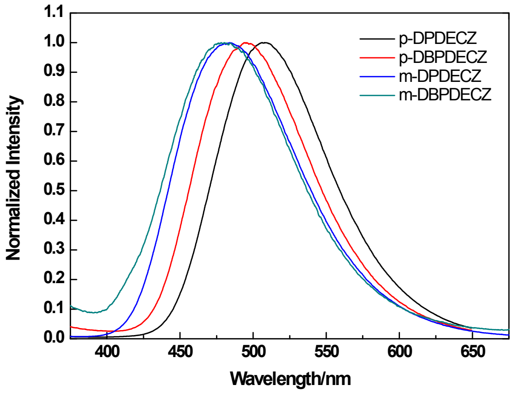


Figure S4. Normalized solid fluorescence spectra of the four AIE luminogens

2.4 Electrochemical Properties

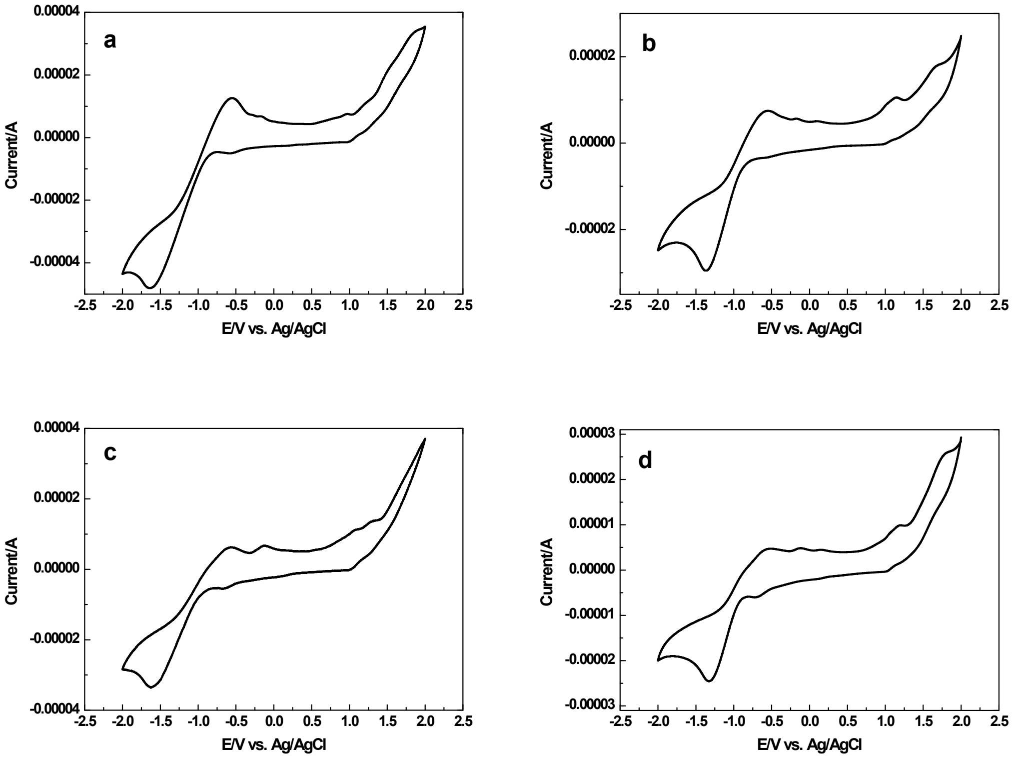


Figure S5. Cyclic voltammogram of p-DPDECZ (a), p-DBPDECZ (b), m-DPDECZ (c) and m-DBPDECZ (d)