

Supporting Information

Efficient Bipolar AIE Emitter for High-Performance Nondoped OLED

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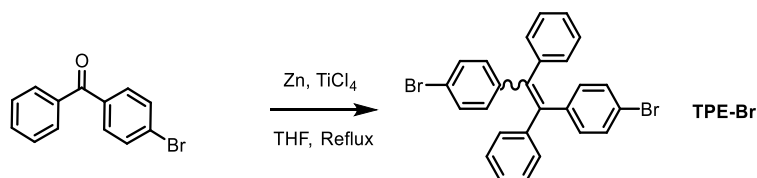
†These two author contributed equally.

1. Materials and Instrumentations

All chemicals applied into reaction were received without further purification. Only titanium(IV) chloride was purchased from Alfa Aesar, while all the other chemicals, including 9-phenyl-9*H*-carbazol-3-ylboronic acid (CAS No. : 854952-58-2), (4-(1-Phenyl-1*H*-benzo[*d*]imidazol-2-yl) phenyl) boronic acid (CAS No.: 952514-79-3), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄), 4-bromobenzophenone, potassium carbonate, and benzophenone were supplied by Energy-Chemicals.

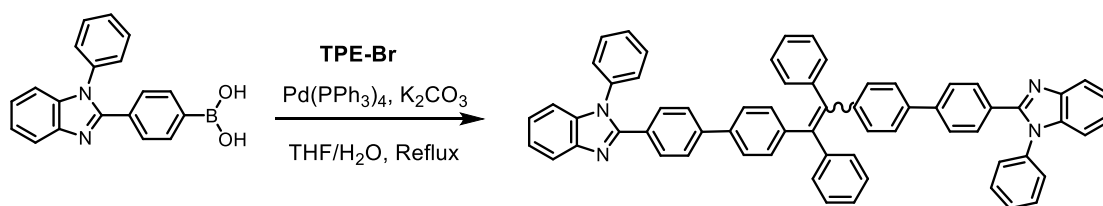
¹H (400MHz) and ¹³C (100MHz) NMR (nuclear magnetic resonance) spectra were recorded through a Bruker DMX-400 Spectrometer (400MHz) using CDCl₃ as solvent and TMS as internal reference. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris Diamond TG/DTA thermal analysis instrument from 30 °C to 650 °C at a scanning rate of 10 °C min⁻¹ under nitrogen. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris Diamond Differential Scanning Calorimeter at a heating rate of 10 °C min⁻¹ from 30 °C to 300 °C under a nitrogen atmosphere. The UV-vis absorption spectra were measured by a Perkin-Elmer

Lambda 950 spectrophotometer. Photoluminescent (PL) spectra were measured on a Fluoromax-4 fluorescence spectrophotometer. Photoluminescent quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaaurus_QY with doped films spinning coated on quartz glass. The DFT calculations were performed with the Gaussian09 series of programs using the B3LYP hybrid functional and 6-31G (d, p) basis set. Electrochemical cyclic voltammetry (CV) was performed on a CHI 660D electrochemical workstation to measure the HOMO level in anhydrous acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile at a scan rate of 100 mv S⁻¹, using Ag/AgCl and platinum wire as reference and counter electrode, respectively. A platinum electrode coated with thin molecule film was used as the working electrode.



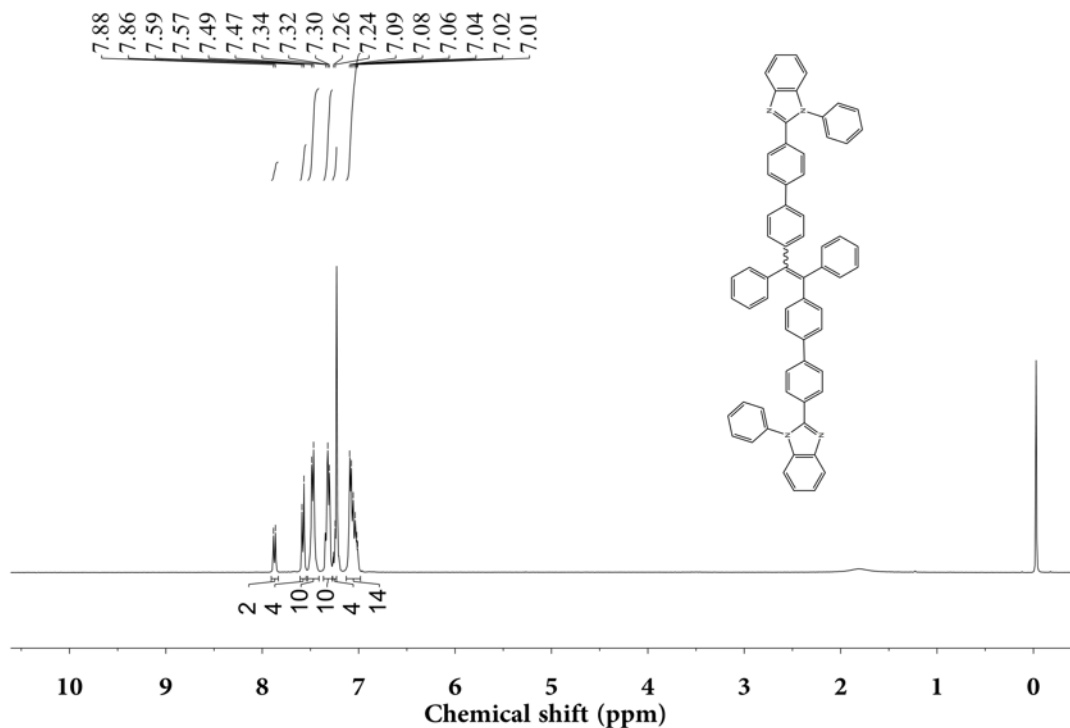
Scheme S1. Synthesis route to AIE precursor **TPE-Br**.

1,2-bis(4-bromophenyl)-1,2-diphenylethene (**TPE-Br**) : TiCl₄ (3.3 mL, 30.0 mmol) was firstly added dropwisely into the mixture of Zn (3.90 g, 60.0 mmol), 4-bromobenzophenone (0.85 mg, 2.5 mmol) and 40 mL dry THF under nitrogen atmosphere at 0 °C. The mixture was stirred for 30 min at room temperature and then refluxed overnight. After that, the mixture was filtrated, extracted with CH₂Cl₂ and finally purified by silica gel chromatography with chloroform and petroleum as eluent to afford a bright yellow solid (1.12 g, 76.2%). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 6.87, 6.99, 7.10, 7.20. ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 120.6, 126.9, 127.7, 128.0, 130.8, 131.2, 132.8, 140.2, 142.3, 142.7. ESI-TOF-MS (C₂₆H₁₈Br₂): m/z 487.9794 (M⁺ calculated 487.9775).

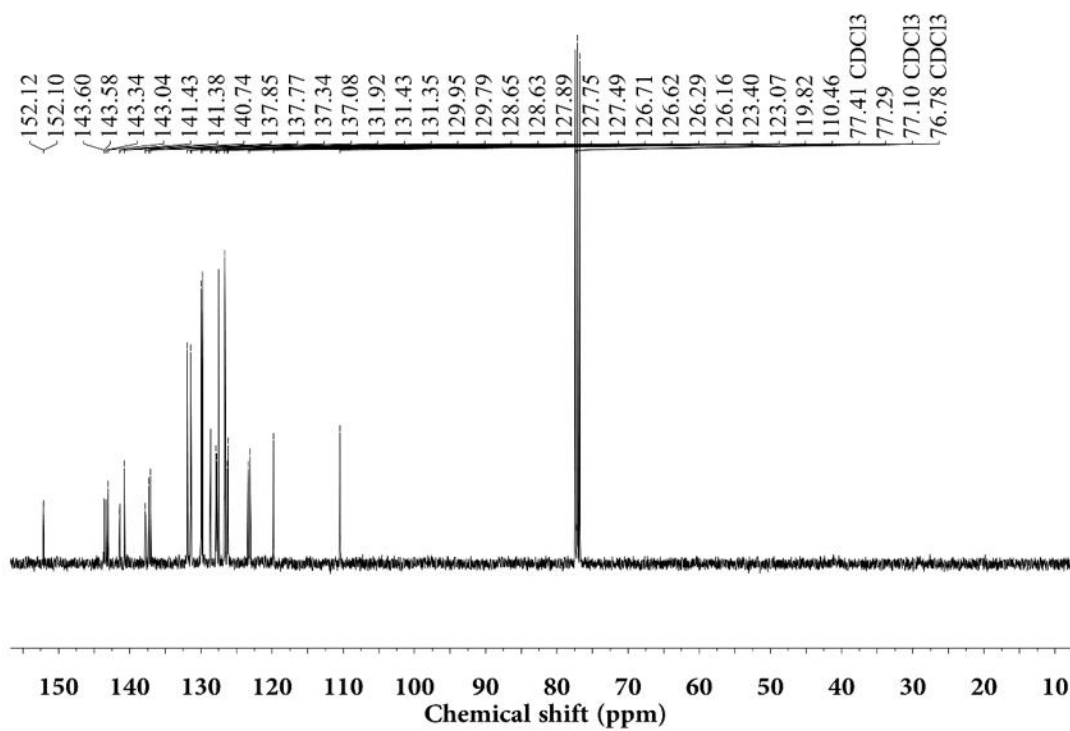


Scheme S2. Synthesis route to **TPE-3**.

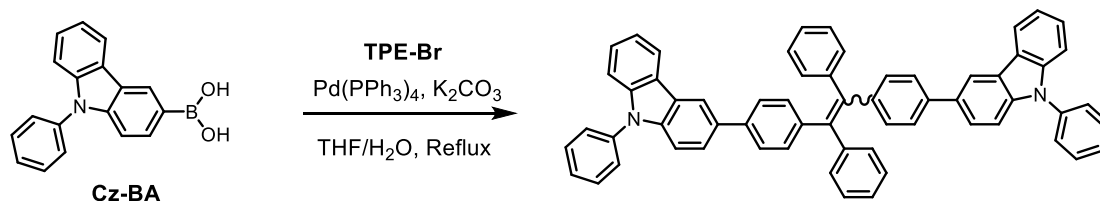
1,2-diphenyl-1,2-bis(4'-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl) ethene (**TPE-3**): 4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenylboronic acid (2.21g, 7.03mmol), 1,2-bis(4-bromophenyl)-1,2-diphenylethene (1.64g, 3.45mmol), K_2CO_3 (9.26g, 70.00mmol), Tetrakis(triphenylphosphine)palladium (486mg, 0.42mmol), THF:H₂O (240mL, 3:1, v/v) were added into a 500 mL 3 neck round bottom flask under nitrogen. The mixture was stirred at 150 °C for 16 hours and then poured into 300mL water, extraction with dichloromethane(DCM), The crude product was purified by column chromatography on silica gel (petroleum ether : dichloromethane = 2:1, v/v) to get 1.20 g of yellow powder in yield of 40 %. ¹H NMR (400 MHz, Chloroform-d) δ 7.87 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.3 Hz, 4H), 7.48 (d, J = 8.0 Hz, 10H), 7.31 (d, J = 6.4 Hz, 10H), 7.24 (s, 4H), 7.12 – 6.99 (m, 14H). ¹³C NMR (101 MHz, Chloroform-d) δ 143.34, 143.04, 140.74, 137.34, 137.08, 131.92, 131.43, 129.95, 129.79, 128.65, 128.63, 127.89, 127.75, 127.49, 126.71, 126.62, 126.29, 126.16, 123.40, 123.07, 119.82, 110.46.



The $^1\text{H NMR}$ spectrum of **TPE-3**

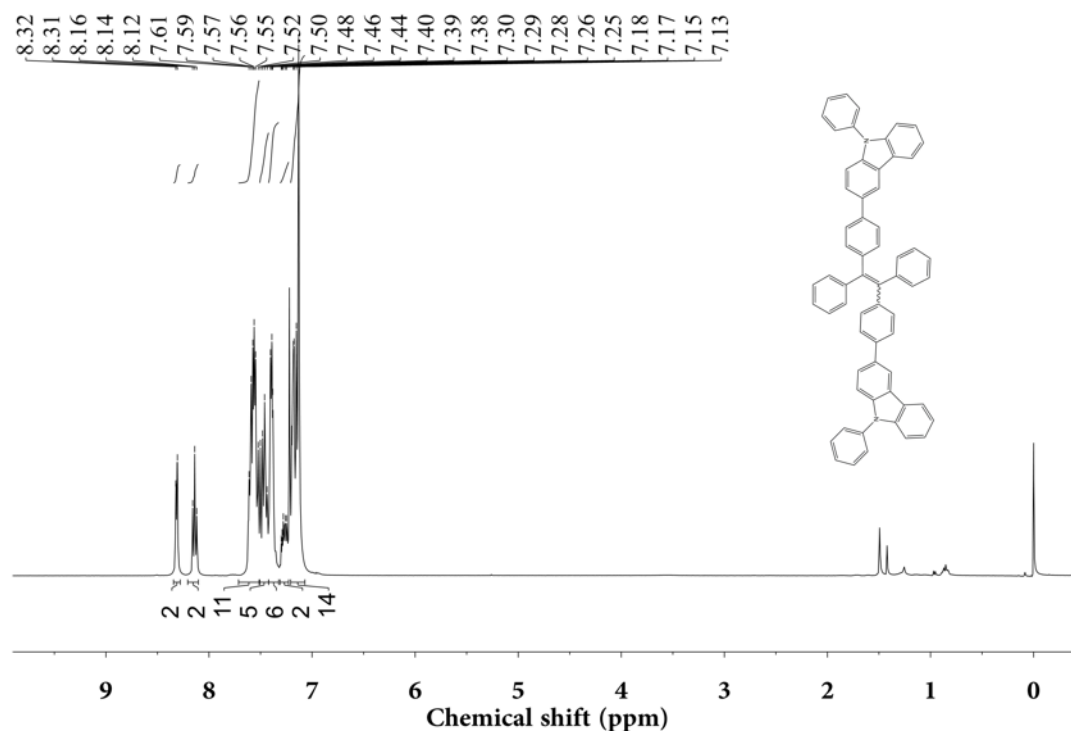


The $^{13}\text{C NMR}$ spectrum of **TPE-3**

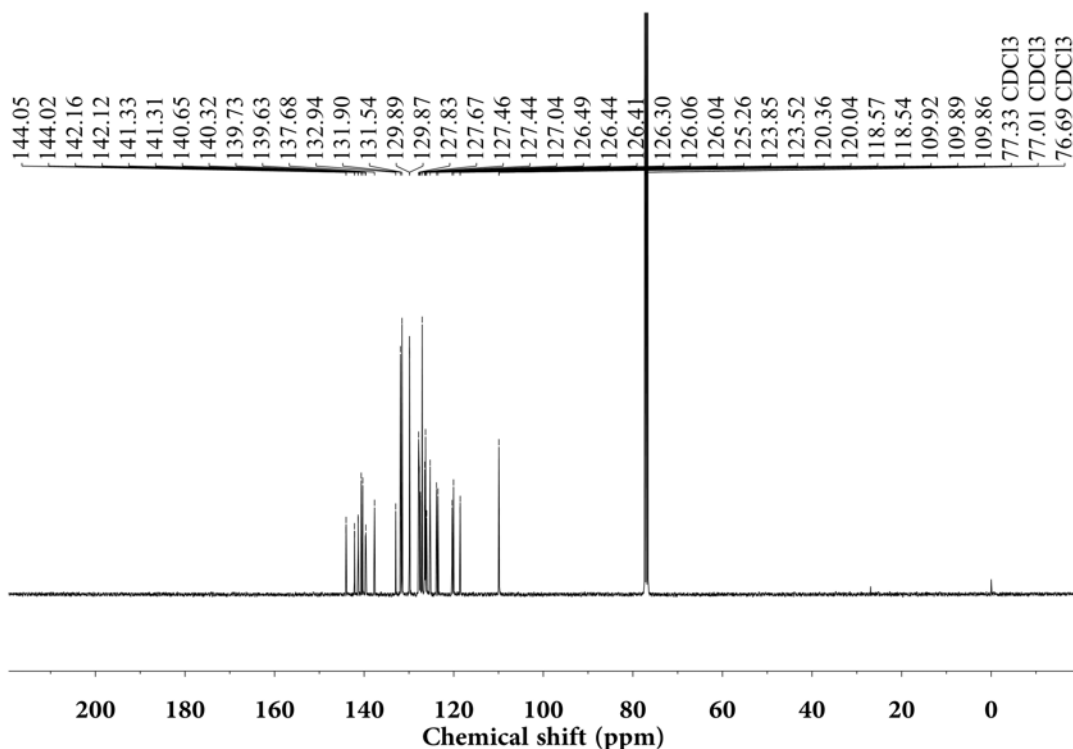


Scheme S3. Synthesis route to **TPE-1**

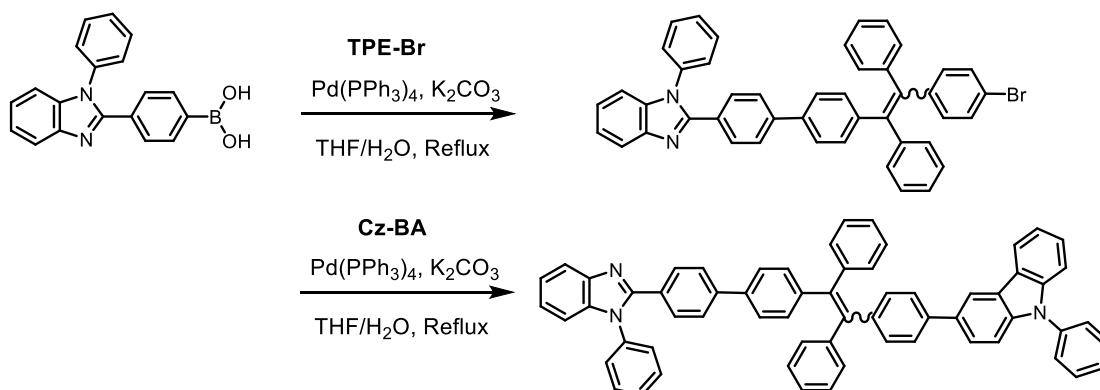
1,2-diphenyl-1,2-bis(4-(9-phenyl-9H-carbazol-3-yl)phenyl)ethene (**TPE-1**): The synthesis of **TPE-1** was similar to that of **TPE-3**. It was obtained as a yellow powder in yield of 54 %. ¹H NMR (400 MHz, Chloroform-d) δ 8.31 (d, J = 6.3 Hz, 2H), 8.14 (t, J = 7.8 Hz, 2H), 7.65 – 7.51 (m, 11H), 7.51 – 7.42 (m, 5H), 7.42 – 7.36 (m, 6H), 7.30 – 7.24 (m, 2H), 7.21 – 7.10 (m, 14H). ¹³C NMR (101 MHz, Chloroform-d) δ 141.31, 140.65, 140.32, 137.68, 132.94, 131.90, 131.54, 129.89, 129.87, 127.83, 127.67, 127.46, 127.44, 127.04, 126.49, 126.44, 126.41, 126.30, 126.06, 126.04, 125.26, 123.85, 123.52, 120.36, 120.04, 118.57, 118.54, 109.92, 109.89, 109.86.



The ¹H NMR spectrum of **TPE-1**



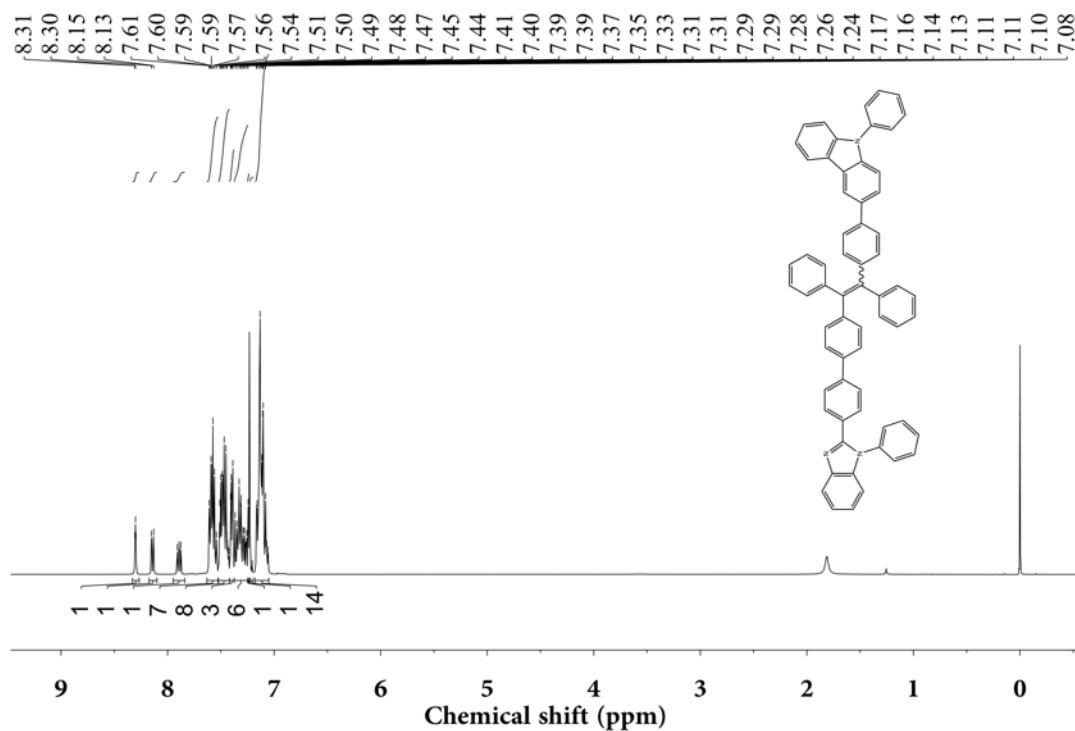
The ^{13}C NMR spectrum of **TPE-1**



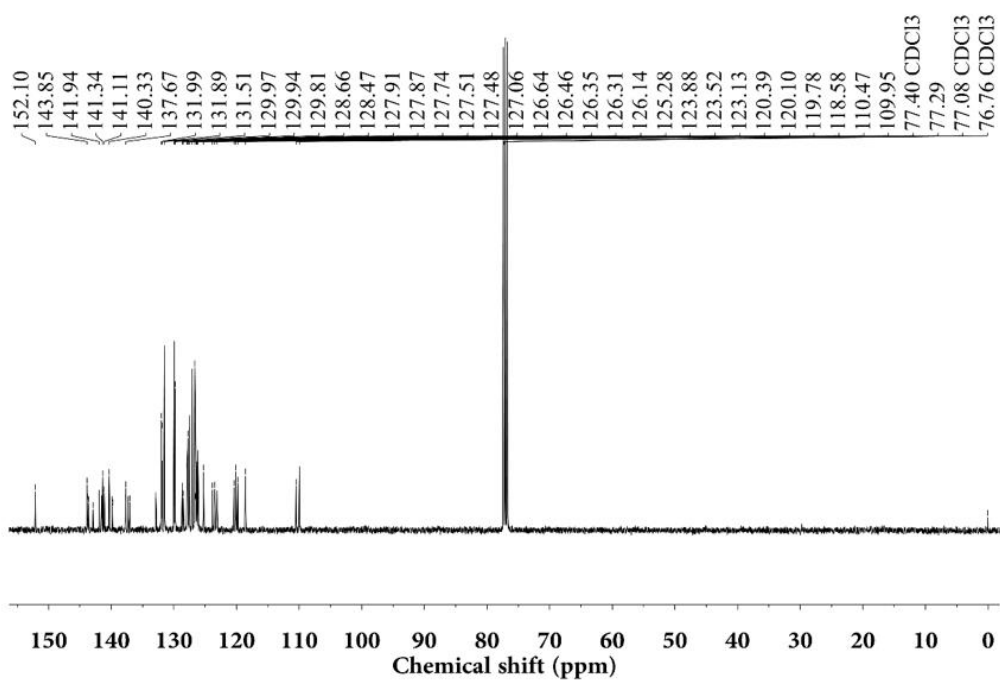
Scheme S4. Synthesis route to **TPE-2**

3-(4-(1,2-diphenyl-2-(4'-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl) vinyl) phenyl)-9-phenyl-9H-carbazole (**TPE-2**): The synthesis **TPE-2** was also similar to that of **TPE-3**. It was obtained as a yellow powder in yield of 33 %. ^1H NMR (400 MHz, Chloroform-d) δ 8.34 – 8.28 (m, 1H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.95 – 7.85 (m, 1H), 7.63 – 7.53 (m, 7H), 7.52 – 7.42 (m, 8H), 7.40 (dd, $J = 6.3, 2.3$ Hz, 3H), 7.37 – 7.25 (m, 6H), 7.24 (s, 1H), 7.21 (s, 1H), 7.18 – 7.04 (m, 14H). ^{13}C NMR (101 MHz, Chloroform-d) δ 152.10, 143.85, 142.89, 141.94, 141.34, 141.11, 140.33, 137.67, 131.99, 131.89, 131.51, 129.97, 129.94, 129.81, 128.66, 128.47, 127.91, 127.87,

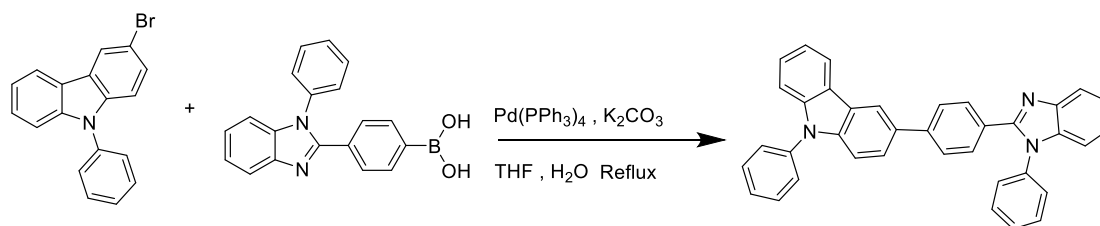
127.74, 127.51, 127.48, 127.06, 126.64, 126.55, 126.46, 126.35, 126.31, 126.14, 125.28, 123.88, 123.52, 123.43, 123.13, 120.39, 120.10, 119.78, 118.58, 110.47, 109.95, 77.29.



The ^1H NMR spectrum of **TPE-2**

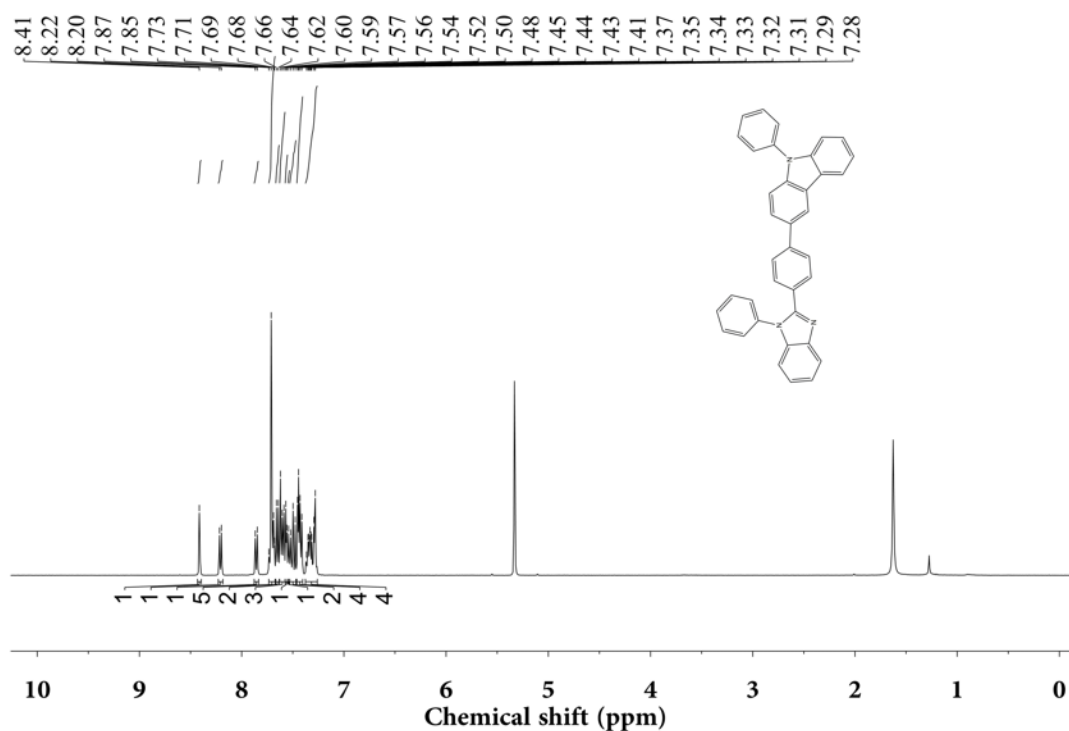


The ^{13}C NMR spectrum of **TPE-2**

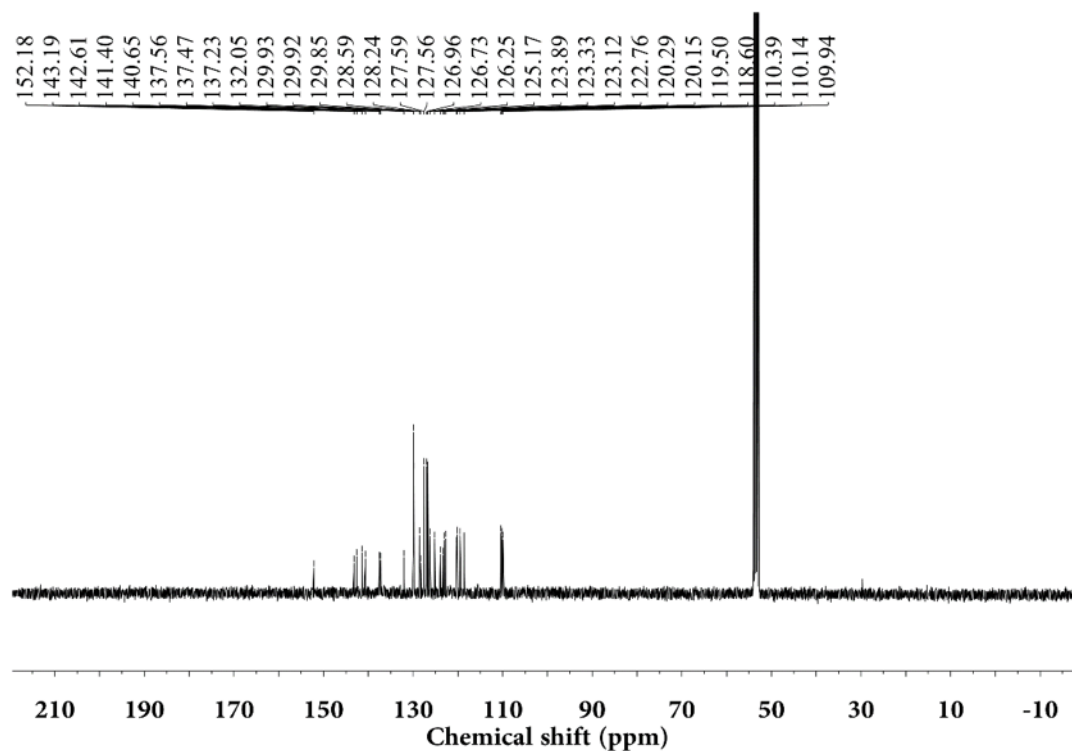


Scheme S5. Synthesis route to **Cz-PBi**

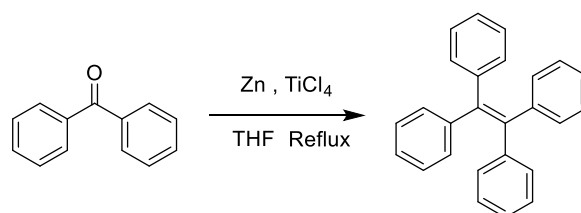
9-phenyl-3-(4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-9H-carbazole (**Cz-PBi**):
 The synthesis of 9-phenyl-3-(4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-9H-carbazole (**Cz-PBi**) was similar to that of **TPE-3**. It was obtained as a white powder in yield of 39 %. ^1H NMR (400 MHz, Chloride- d_2) δ 8.34 – 8.28 (m, 1H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.95 – 7.85 (m, 1H), 7.63 – 7.53 (m, 7H), 7.52 – 7.42 (m, 8H), 7.40 (dd, $J = 6.3, 2.3$ Hz, 3H), 7.37 – 7.25 (m, 6H), 7.24 (s, 1H), 7.21 (s, 1H), 7.18 – 7.04 (m, 14H). ^{13}C NMR (101 MHz, Methylene Chloride- d_2) δ 143.19, 141.40, 140.65, 137.56, 137.23, 132.05, 129.93, 129.92, 129.85, 128.59, 128.24, 127.59, 127.56, 126.96, 126.73, 126.25, 125.17, 123.89, 123.33, 123.12, 122.76, 120.29, 120.15, 119.50, 118.60, 110.39, 110.14, 109.94.



The ^1H NMR spectrum of **Cz-PBi**

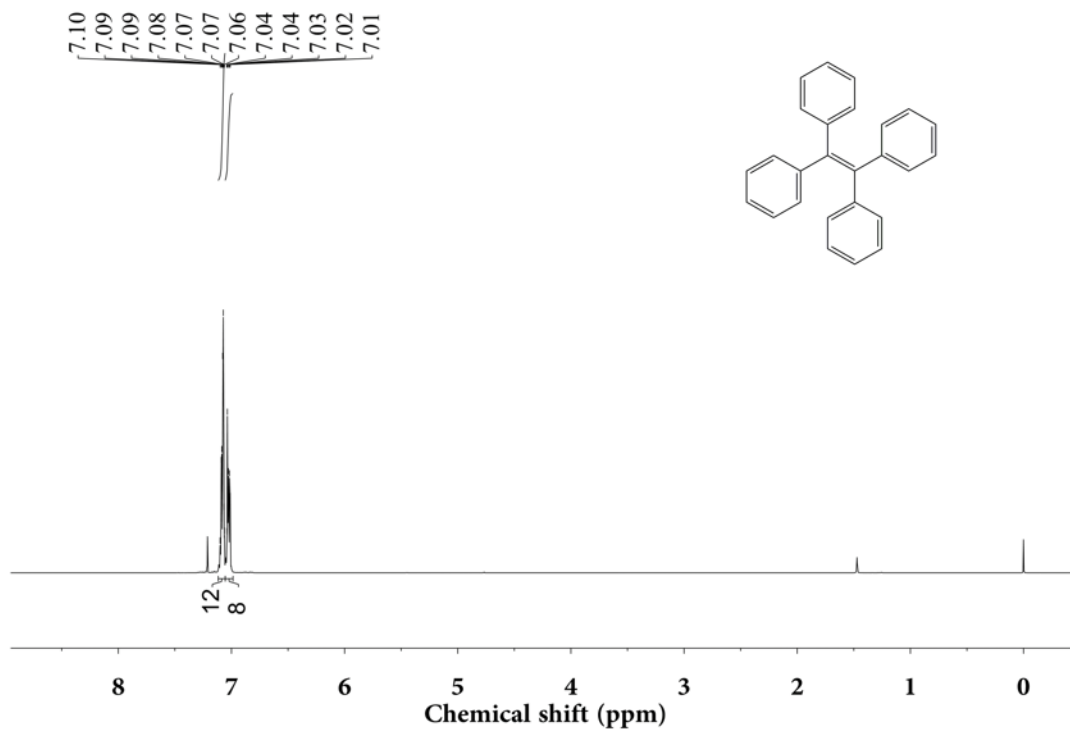


The ^{13}C NMR spectrum of **Cz-PBi**

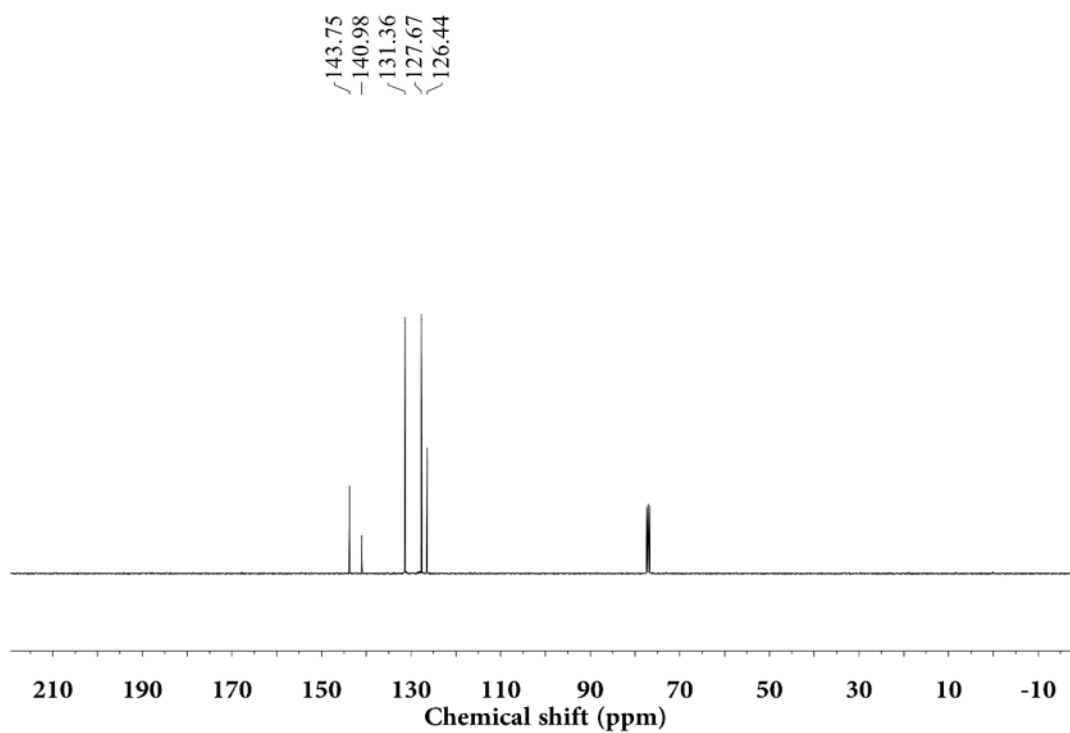


Scheme S6. Synthesis route to **TPE**

Tetraphenylethene (**TPE**): The TPE was synthesized through McMurry reactions, according to previous research.¹



The ^1H NMR spectrum of **TPE**



The ^{13}C NMR spectrum of **TPE**

2. Thermal Analysis of AIEgens

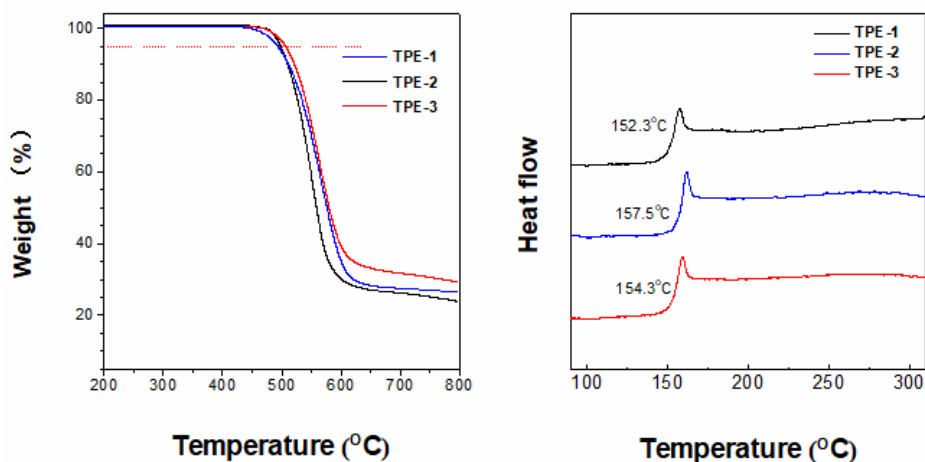


Figure S1. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) curves **TPE-n** ($n=1-3$).

3. Optical Properties of AIEgens

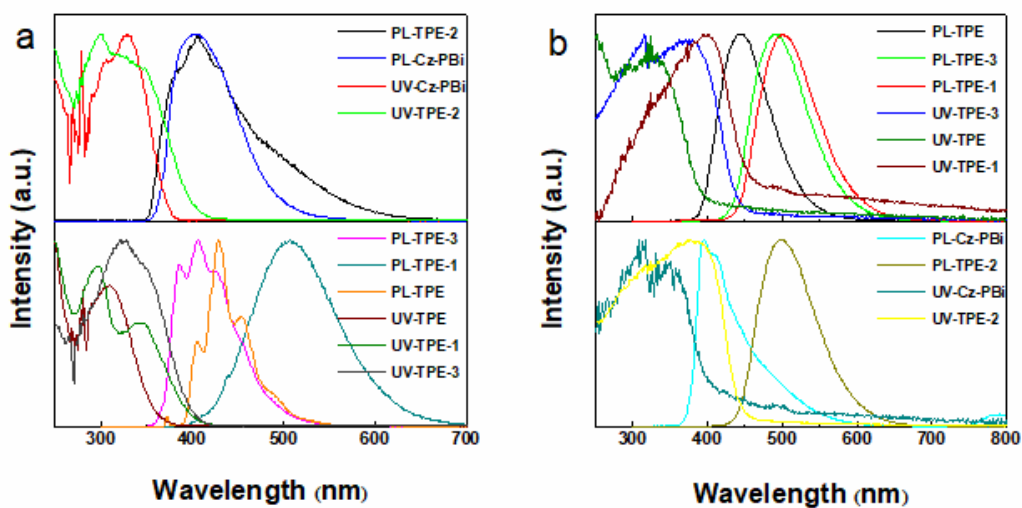


Figure S2. The photoluminescence in THF (a) and film (b), based on **Cz-PBi**, **TPE** and its derivatives **TPE-n** ($n=1-3$).

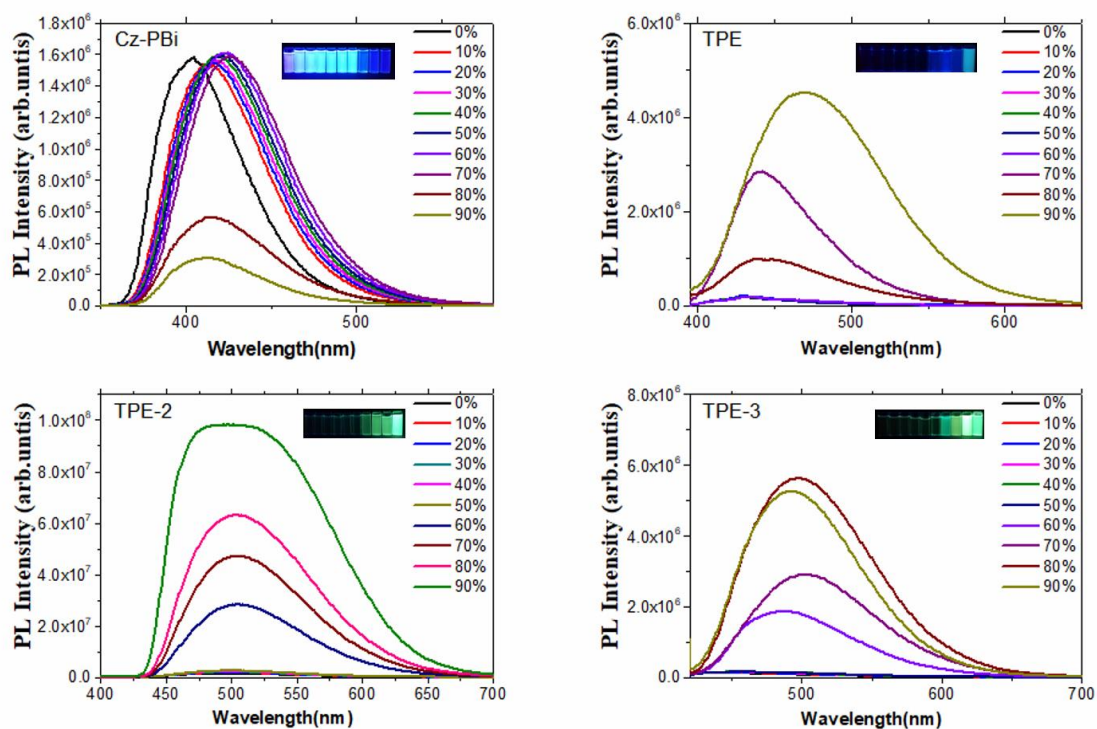


Figure S3. PL spectra in THF/water mixture with different water fraction (fw%) of Cz-PBi, TPE, TPE-2 and TPE-3.

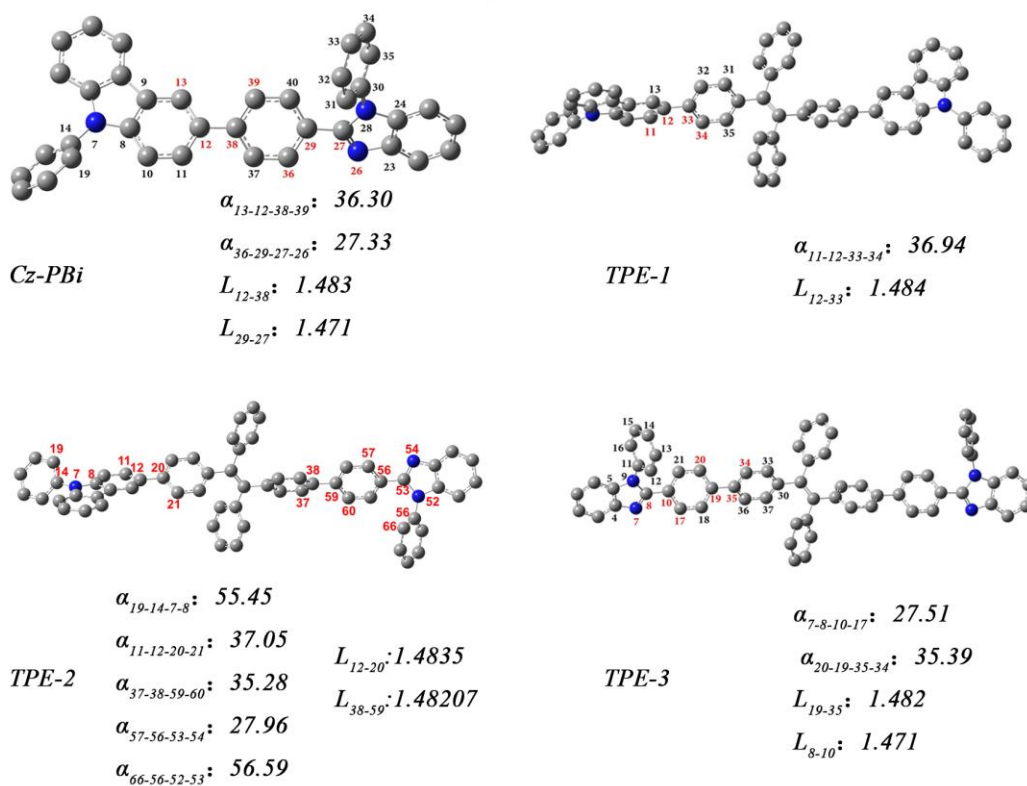


Figure S4. Optimized structures of Cz-PBi, TPE and TPE-n (n=1-3).

4. Electrochemical Properties of AIEgens

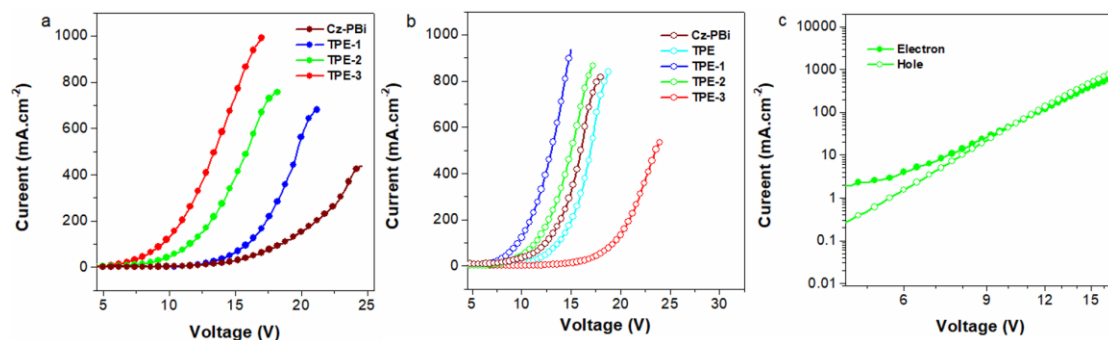


Figure S5. The current density-voltage characteristics of a) electron-only (linear), b) hole-only (linear) devices of the and c) the comparison within TPE-2(double logarithm)

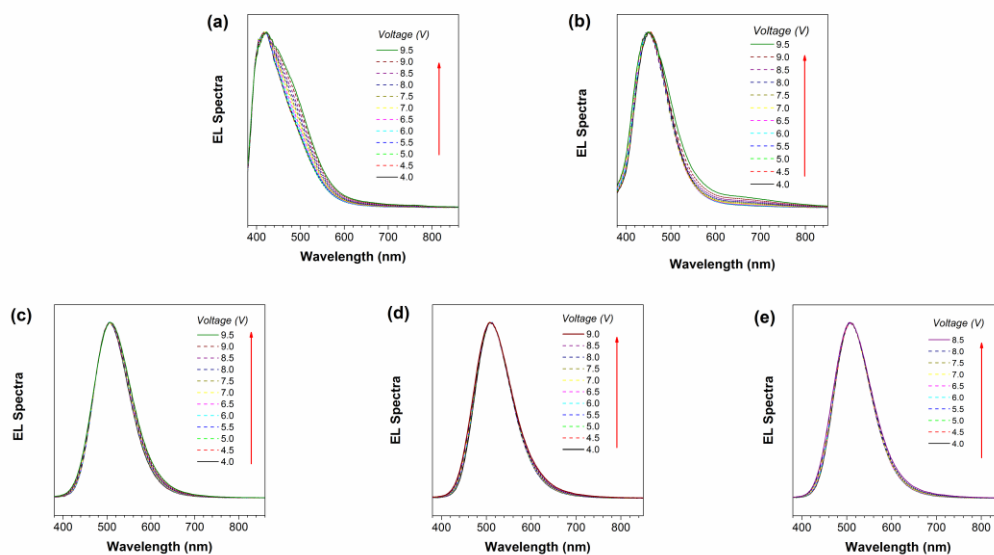


Figure S6. EL spectra of the nondoped OLED devices based on the emitters of (a) Cz-PBi, (b) TPE, (c) TPE-1, (d) TPE-2, and (e) TPE-3 at different working voltages.

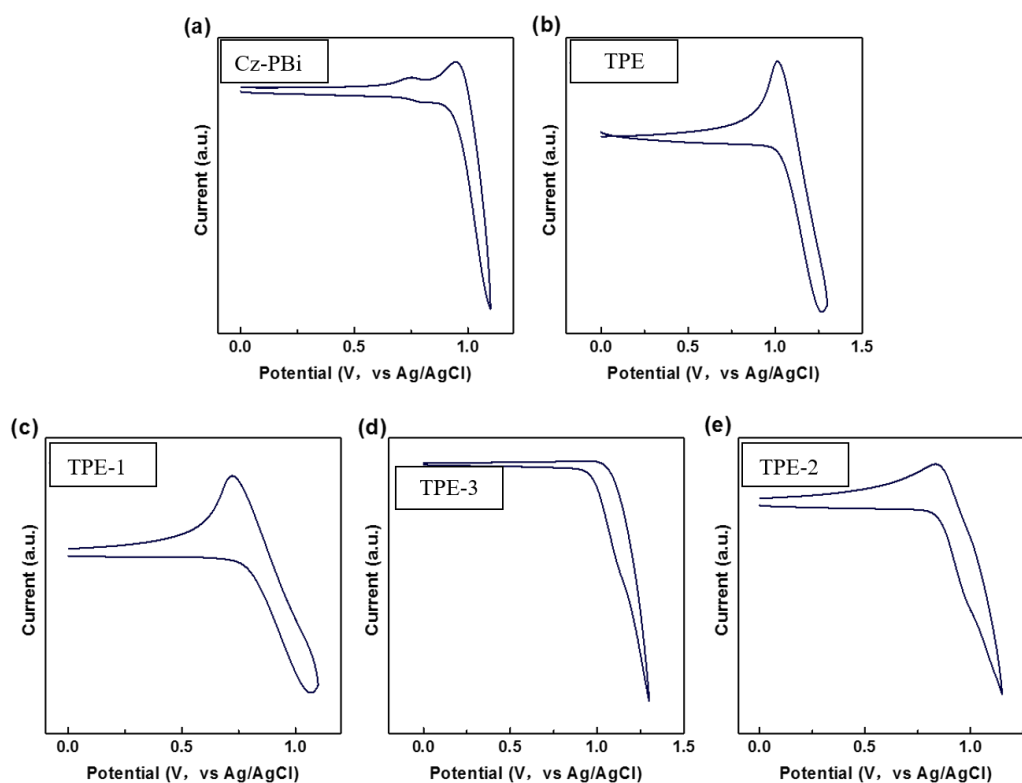


Figure S7. Cyclicvoltammmetry characteristics of (a) Cz-PBi, (b) TPE, (c) TPE-1, (d) TPE-3, and (e) TPE-2

5. OLED Device's Fabrication and Characterization

The materials to fabricate OLED devices were purchased from Jinlin Optical and Electronic Materials Co. The Indium-doped tin oxide (ITO) glass sheet (1.2 mm thick, $\leq 15 \Omega/\text{square}$, transmittance $> 90\%$) was purchased from Nippon Sheet Glass Company, Ltd, and cleaned by a routine cleaning procedure which includes initial manual washed in aqueous detergent, and then sequentially sonication in acetone, isopropanol and ethanol for 30 minutes each. Then, the pre-cleaned ITO glass was moved into an ultraviolet chamber for UV-ozone treatment of 20 minutes. The synthesized emitting materials **TPE 1-3** were further purified through sublimation at 220°C under the vacuum of $1.5 \times 10^{-3} \text{ Pa}$ in the sublimation system (CSe solar ETS-60T-S) before fabricating the OLED devices.

The organic layers were deposited consecutively on the pre-cleaned ITO glass substrates in a vacuum chamber ($5 \times 10^{-4} \text{ Pa}$). The deposition rate of all the organic

materials was $0.9\text{-}1.1\text{ \AA s}^{-1}$, while that of the LiF was 0.1 \AA s^{-1} and aluminum was 5 \AA s^{-1} . The electrical characteristics of the devices were measured with a Keithley 2400 Source meter at the range of 0-15V. The electroluminescence spectra and luminance of the devices were obtained on a PR655 spectrometer in ambient conditions at room temperature.

1. Dong Y, Lam JWY, Qin A, Liu J, Li Z, Tang BZ, et al. Aggregation-induced emissions of tetraphenylethene derivatives and their utilities as chemical vapor sensors and in organic light-emitting diodes. *Applied Physics Letters*. 2007;91(1).