

Supporting Information

Highly efficient organic–inorganic electroluminescence materials for solution-processed blue organic light-emitting diodes

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Experimental Section

Materials

Octakis(dimethylsiloxy)silsesquioxane (Q₈M₈) was purchased from Hybrid Plastics (Hattiesburg, MS, USA). All other chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA) at the highest purity available (> 99%) and used without further purification unless otherwise specified. All organic solvents were high-performance liquid chromatography (HPLC)-grade and purchased from TEDIA (Fairfield, OH, USA). Dimethylmethanamide (DMF) and toluene were vacuum distilled from calcium hydride and subsequently stored over activated molecular sieves prior to use.

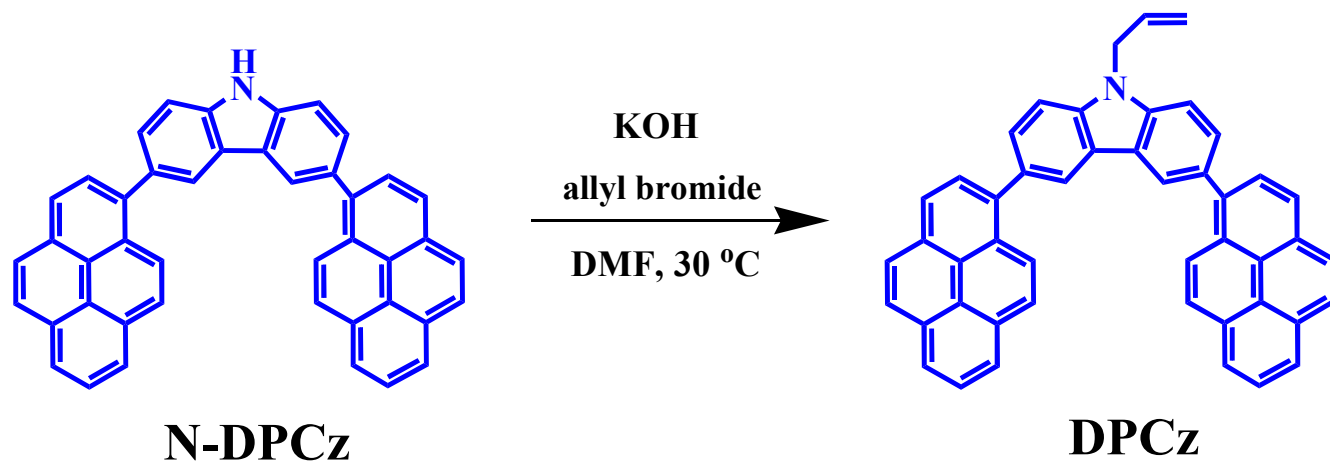
Characterizations

Nuclear magnetic resonance (NMR). ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova

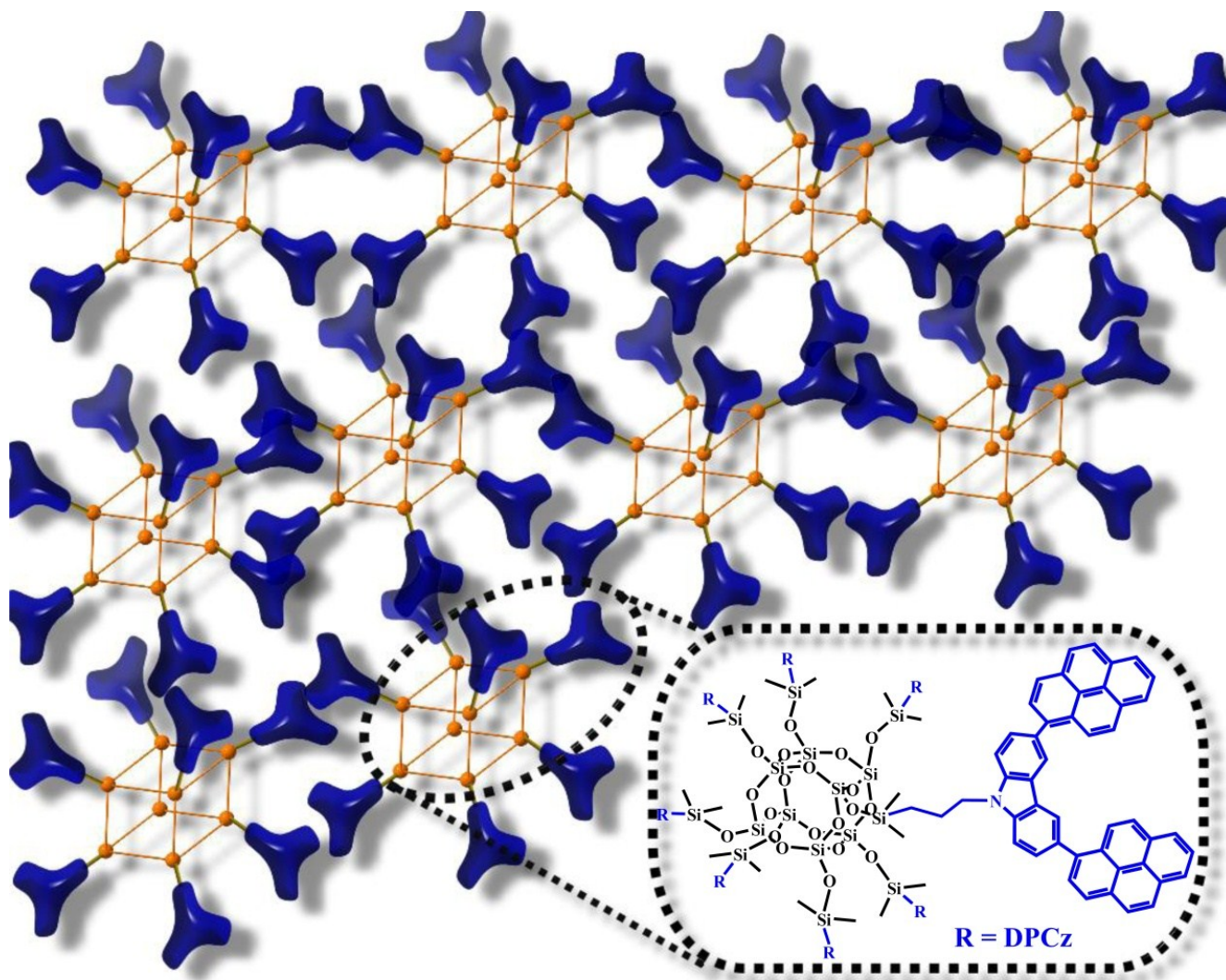
500 MHz spectrometer (Palo Alto, CA, USA) using a nominal field of 9.395 T. *Gas chromatography-mass spectroscopy (GC-MS)*. GC/MS spectra were acquired using a Micromass Trio 2000 mass spectrometer (Micromass, Beverly, MA). *Elemental Analysis (EA)*. EA was performed using a CHN-O-Rapid elemental analyzer (Foss. Heraeus, Germany). *Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy (MALDI-TOF MS)*. MALDI-TOF MS was performed using a Bruker Autoflex II instrument (Billerica, MA, USA) equipped with a nitrogen laser (337 nm) operating at 200 Hz in linear mode over a mass range of 600 to 400000 Daltons. The matrix compound was 2,5-dihydroxy benzoic acid (DHB). *Differential scanning calorimetry (DSC)*. DSC was performed using a PerkinElmer DSC 4000 instrument (Beaconsfield, Buckinghamshire, UK) operated at a scan rate of 10 °C/min over a temperature range from 0 to 250 °C. DSC plots for the second heating scan are presented in **Figure 1a**. *Thermogravimetric analysis (TGA)*. TGA was undertaken using a TA Instruments Q50 apparatus (New Castle, DE, USA). The thermal stabilities of the samples in a nitrogen atmosphere were determined by measuring weight loss while heating at a rate of 20 °C/min from 25 to 800 °C. *Ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectra*. UV-Vis spectra were measured using an HP 8453 diode-array spectrophotometer (Hewlett-Packard, Waldbronn, Germany). PL spectra were obtained using a Hitachi F4500 luminescence spectrometer (Hitachi Co., Ltd., Tokyo, Japan), *Cyclic Voltammetry (CV)*. CV measurements were performed using a BAS 100 B/W (Bioanalytical Systems, Lafayette, IN, USA) electrochemical analyzer operated at a scan rate of 100 mV/s in the presence of tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte in acetonitrile under nitrogen atmosphere. The samples were prepared on an indium tin oxide (ITO) substrate by spin coating in air at a speed of 2000 rpm for 20 s. The measured potentials were recorded with respect to the Ag/Ag⁺ (0.01 M AgNO₃) reference electrode using ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference. The resulting CV spectra are shown in **Figure S5**. *Scanning Electron Microscopy (SEM)*. SEM images were recorded using a field-emission scanning electron microscope (Hitachi S-4700, Tokyo, Japan) at an accelerating voltage of 15 kV. Sample preparation for SEM imaging was spin-coating onto the silicon substrate and then coating with platinum by ion beam sputtering. *Fabrication of OLED Devices*. Devices were fabricated in the following configuration: ITO/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, 35 nm)/emissive layer (ca. 60 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI, 30 nm)/lithium fluoride (LiF, 1.5 nm)/aluminum (Al, 100 nm). The PEDOT:PSS layer was used as a hole injection/transport layer to facilitate hole conduction and to tune energy levels, and also smoothens the rough ITO surface. Then, the emissive layer was spin-coated on the PEDOT:PSS coated ITO substrate at 3000 rpm from the chloroform solutions of POSS-DPCz (or DPCz) and followed by thermal annealing at 120 °C for 30 min in a vacuum oven. The TPBI layer deposited via thermal evaporation was used as an electron transport/hole blocking layer. The cathode was completed through thermal deposition of LiF at

a deposition rate of 0.1 Å/s, then capped with Al metal via thermal evaporation at a rate of 4.0 Å/s. Device performance was characterized using previously described procedures.⁸

Syntheses



Scheme S1: Synthetic procedure for DPCz.



Scheme S2: Graphical representation of well-dispersed POSS nanoparticles formed from POSS-DPCz in the thin-film state.

Synthesis of DPCz

N-dipyrenylcarbazole (*N*-DPCz) was synthesized from pyrene-1-boronic acid and 3,6-diiodo-9*H*-carbazole, as previously described.¹¹ *N*-DPCz (5.67 g, 0.01 mol) was dissolved in DMF (50 ml), powdered potassium hydroxide (1.12 g, 0.02 mol) was added, the mixture was stirred at room temperature for 1 h, a solution of allyl bromide (2.42 g, 0.02 mol) was added slowly via a plastic syringe, stirred for 36 h at room temperature, the reaction mixture was poured into 500 ml of ice-cold water with efficient stirring, then extracted several times with chloroform. The chloroform layer was dried over anhydrous magnesium sulfate. The crude product was purified by flash column chromatography on silica gel (chloroform/hexane = 1/1) to give the final product (5.82 g, 95% yield) as a pale yellow powder. FAB-MS: m/z 608 $[M+H]^+$.

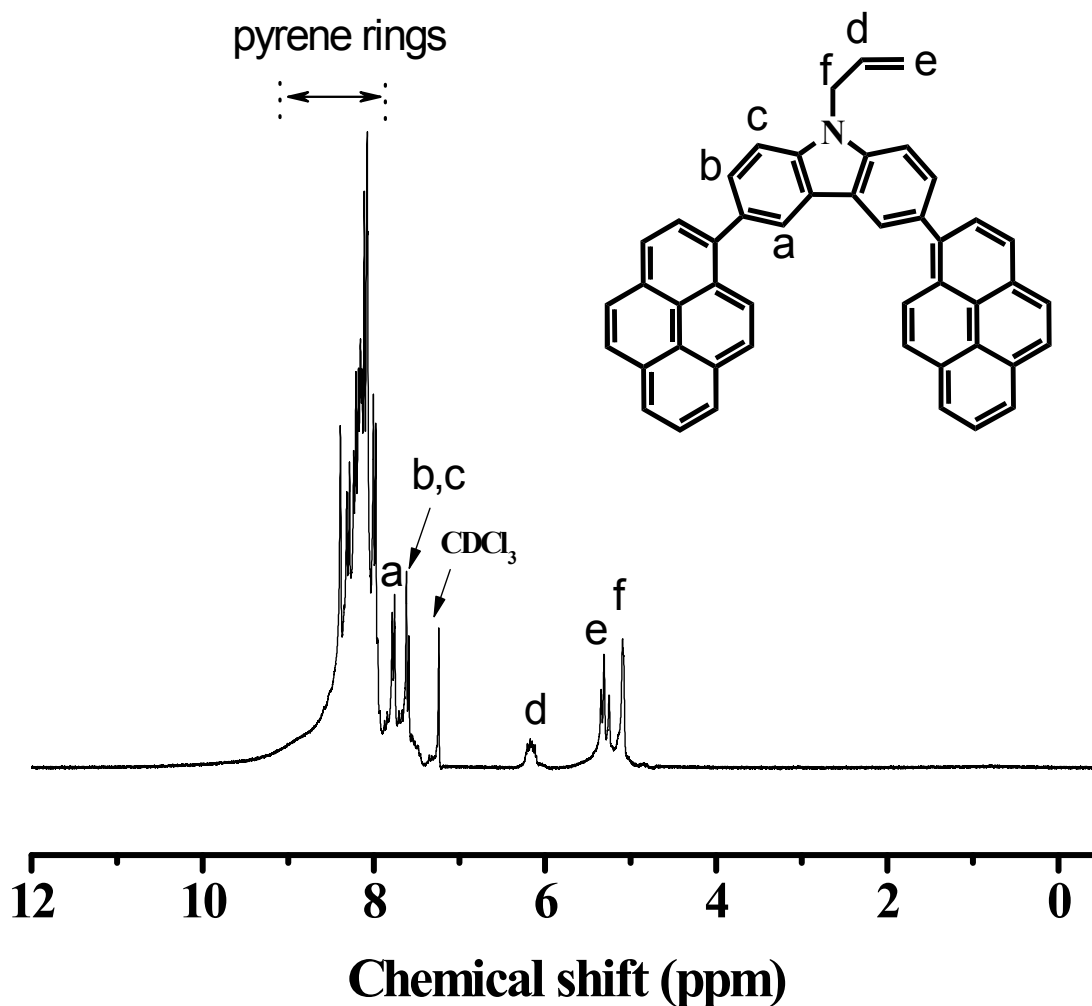


Fig. S1: ^1H NMR spectrum of DPCz in CDCl_3 .

Synthesis of POSS-DPCz

Q_8M_8 (1.02 g, 1.0 mmol) and DPCz (5.46 g, 9.0 mmol) were dissolved in dry toluene (50 ml). A toluene solution of platinum-divinyltetramethyldisiloxane complex catalyst (Pt-dvs, 0.2 ml, 400 ppm) was injected into the mixed solution using a microsyringe. The mixture was stirred at 80 °C under a nitrogen atmosphere until the Si–H peak (2140 cm^{-1}) disappeared completely (ca. 3 h), as observed by Fourier transform infrared spectroscopy. After cooling to room temperature, the mixture was filtered, further purified by extraction in a Soxhlet extractor with refluxing methanol for 2 days, and then dried under vacuum to yield POSS-DPCz (5.12 g, 87%); MALDI-TOF MS: m/z 5896 $[\text{M} + \text{Na}]^+$

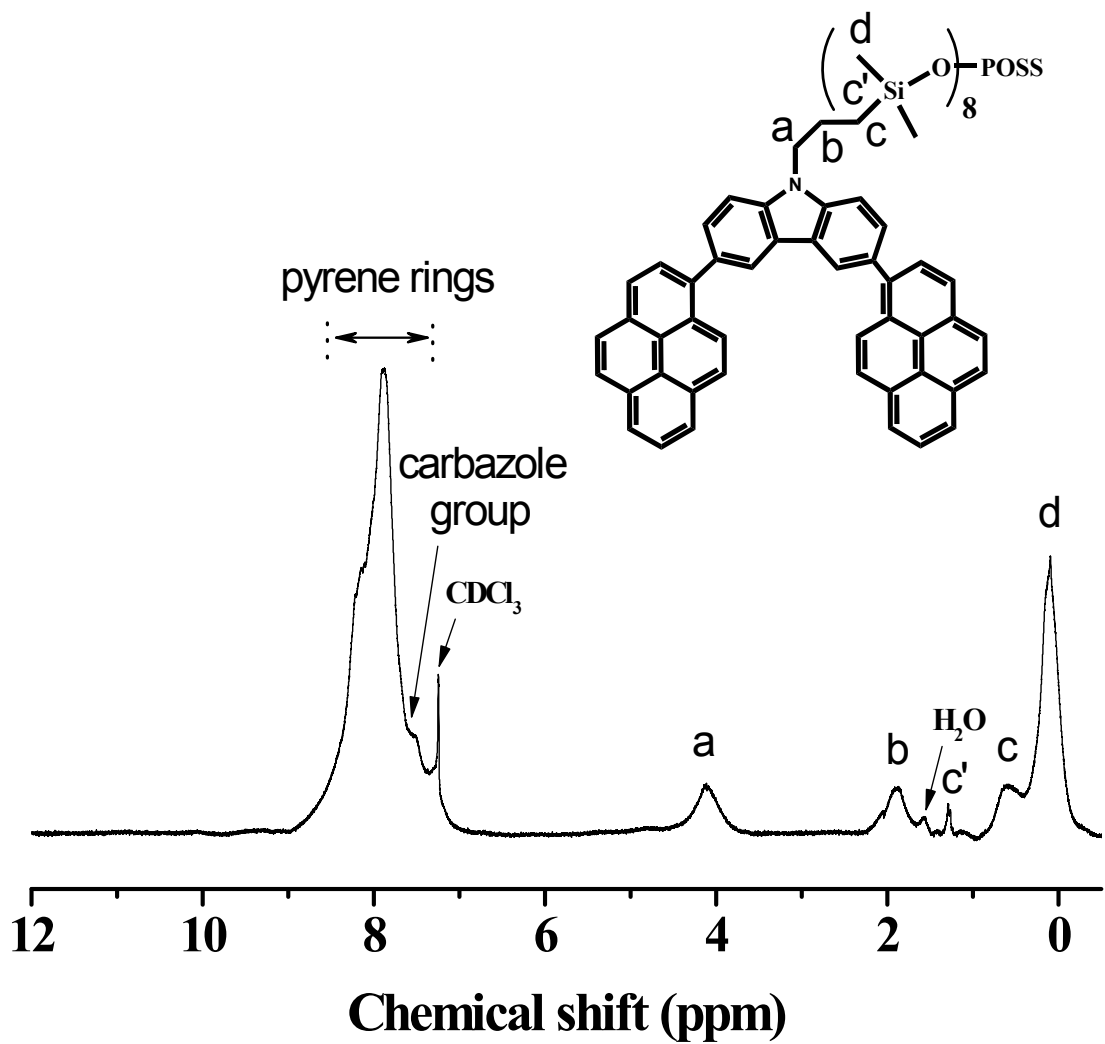


Fig. S2: ^1H NMR spectrum of POSS-DPCz in CDCl_3 .

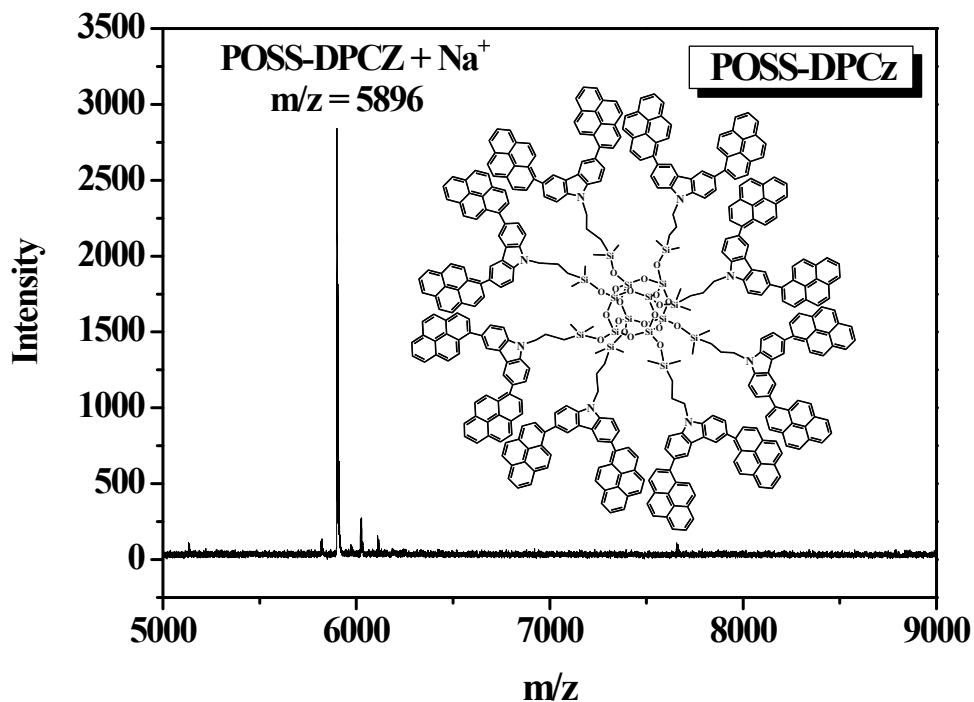


Fig. S3: MALDI-TOF mass spectrum of POSS-DPCz.

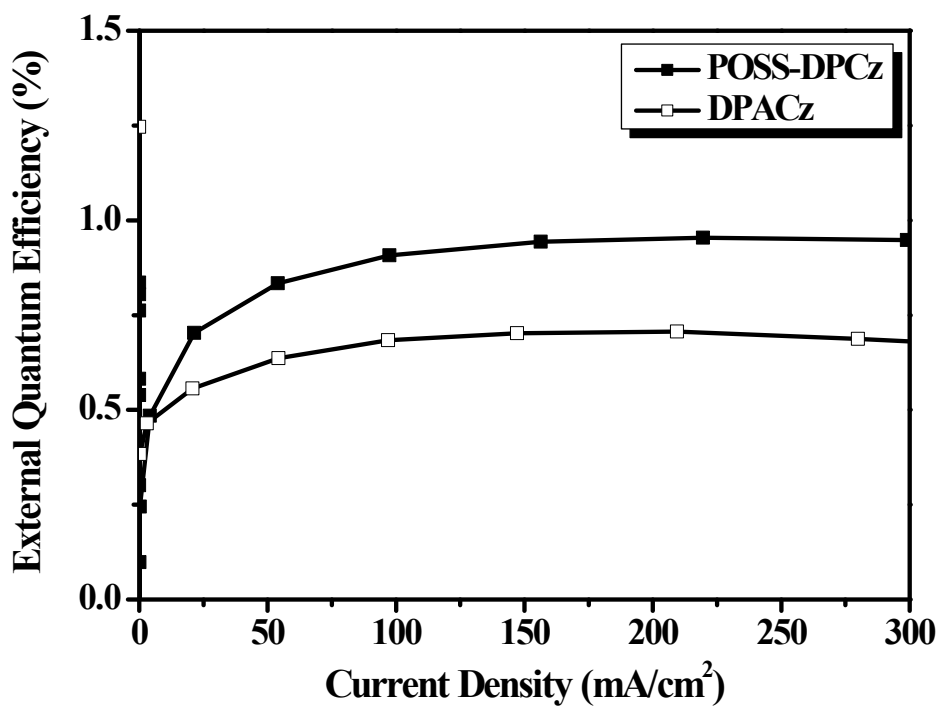


Fig. S4: Plot of external quantum efficiency with respect to current density for the ITO/PEDOT:PSS/emissive layer/TPBI/LiF/Al devices.

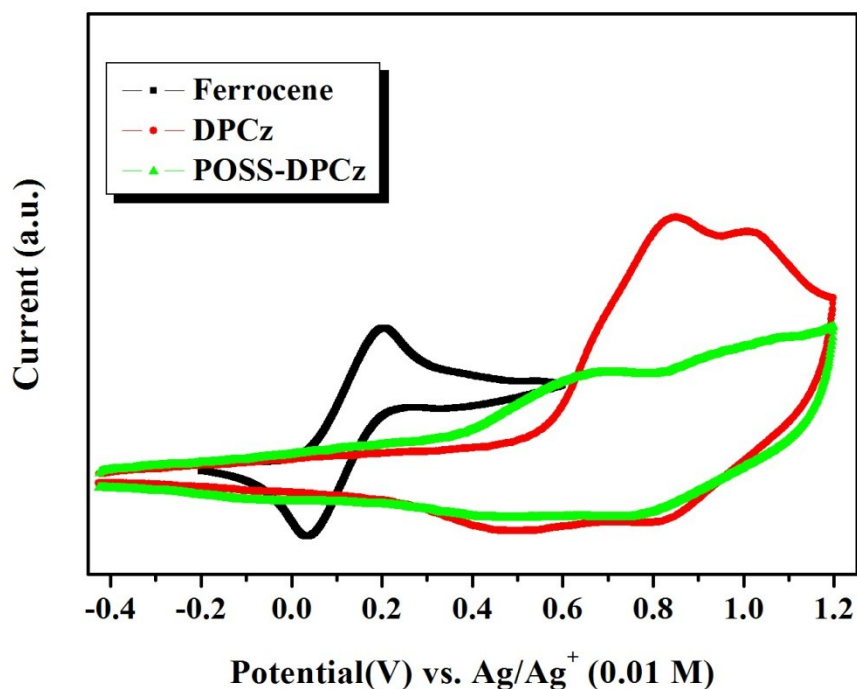


Fig. S5: Cyclic voltammograms of POSS-DPCz, DPCz and ferrocene in acetonitrile.

Table S1. Performance data of device based on structure ITO/PEDOT:PSS/emissive layer/TPBI/LiF/Al devices.

Emissive layers	V_{on}^{a} (V)	$Q_{\text{max}}^{\text{b}}$ (%)	$LE_{\text{max}}^{\text{c}}$ (cd/A)	$B_{\text{max}}^{\text{d}}$ (cd/m ²)	$VB_{\text{max}}^{\text{e}}$ (V)
DPACz	4.8	0.71	0.8	4630	10.5
POSS-DPCz	4.5	0.92	1.4	8900	11.0

^a Turn-on voltage (defined as the bias voltage at 1 cd/m²). ^b Maximum external quantum efficiency. ^c Maximum luminous efficiency. ^d Maximum brightness. ^e Driving voltage corresponding to maximum brightness.