Electronic Supplementary Information (ESI)

# A six-carbazole-decorated cyclophosphazene as a host with high triplet energy to realize highly efficient delayed-fluorescence OLEDs

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**General.** <sup>1</sup>H NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR signals were quoted to tetramethylsilane ( $\delta = 0.00$ ) and CDCl<sub>3</sub> ( $\delta$  = 77.0) as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analyses were carried out with a Yanaco MT-5 CHN corder. UV/Vis absorption and photoluminescence (PL) spectra were measured with a Shimadzu UV-2550 spectrometer and a Horiba Fluoromax-4 spectrophotometer, respectively. PL quantum yields were measured using an integration sphere system coupled with a photonic (Hamamatsu Photonics C9920-02, multichannel analyzer PMA-11). The luminescence intensity and lifetime of solutions and thin films were measured with a Quantaurus-Tau (Hamamatsu Photonics). The HOMO energy levels were determined using a Riken-Keiki AC-3 ultraviolet photoelectron spectrometer. The LUMO energy levels were estimated by subtracting the optical energy gap  $(E_g)$  from the measured HOMO energy levels; the  $E_g$  values were determined from the onset position of the absorption spectra. The density-functional theory (DFT) calculations were performed on the Gaussian 03 program package, using the B3LYP functional with the 6-31G(d) basis set.<sup>1</sup> Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DTG-60AH at a scanning rate of 10 °C min<sup>-1</sup> and a Netzsch DSC204 Phoenix calorimeter at a scanning rate of 5 °C  $min^{-1}$ , respectively, under N<sub>2</sub> atmosphere. AFM was performed using a JEOL JSPM-5400 scanning probe microscope with tapping-mode in air. X-ray crystallographic analyses were made on a Rigaku VariMax with a Saturn 724+ system with graphite monochromated  $MoK\alpha$  radiation. The structures were solved by direct methods (SIR2008)<sup>2</sup> and refined by full-matrix least-square techniques based on  $F^2$ (SHELXL-97).<sup>3</sup>

**OLED Device Fabrication and Measurements.** ITO-coated glass substrates were cleansed with detergent, deionized water, acetone, and isopropanol, followed by UV-ozone treatment. Organic layers and metal electrodes were deposited by high-vacuum thermal evaporation onto the ITO substrates. The layer thickness and the deposition rate were monitored in situ during the deposition by an oscillating quartz thickness monitor. The current density–voltage–luminance characteristics of the devices were measured using a semiconductor parameter analyzer (Agilent E5273A) and an optical powermeter (Newport 1930-C).

**Materials and Syntheses.** Commercially available reagents and solvents were used without further purification unless otherwise noted. All of the reactions were performed under a nitrogen atmosphere in dry solvents.

**Synthesis of hexakis**(*9H*-carbazol-9-yl)cyclotriphosphazene (PzCz). To a stirred solution of NaH (0.72 g, 30.0 mmol) in dry DMF (100 mL) was added a solution of carbazole (4.01 g, 24.0 mmol) in dry DMF (50 mL) at 0 °C, and the mixture was allowed to react for 20 min at that temperature. Hexachlorocyclotriphosphazene (P<sub>3</sub>N<sub>3</sub>Cl<sub>6</sub>, 1.04 g, 3.0 mmol) was then added, and the mixture was stirred for 7 days at 110 °C. The reaction mixture was poured into methanol to form a precipitate. The precipitate was collected by filtration and washed with water and methanol. The product was purified by silica gel column chromatography (eluent: CHCl<sub>3</sub>), and dried under vacuum to afford PzCz as a white solid (yield = 1.74 g, 54%). This compound was further purified by temperature-gradient sublimation before use. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.94 (d, *J* = 8.0 Hz, 12H), 7.50 (*d*, J = 8.5 Hz, 12H), 7.10 (t, *J* = 7.5 Hz, 12H), 6.57 (br, 12H). MS (MALDI-TOF): *m/z* 1132.2 [*M* + H]<sup>+</sup>. Anal. calcd (%) for C<sub>72</sub>H<sub>48</sub>N<sub>9</sub>P<sub>3</sub>: C 76.38, H 4.27, N 11.13; found: C 76.40, H 4.20, N 11.14.

**Synthesis of 2,5-bis(carbazol-9-yl)-1,4-dicyanobenzene (CzTPN).** A mixture of 2,5-dibromo-1,4-dicyanobenzene<sup>4</sup> (1.44 g, 5.0 mmol), carbazole (1.89 g, 11.3 mmol), capper (0.64 g, 10.0 mmol), 18-crown-6 (0.26 g, 0.1 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.79 g, 20.0 mmol) in dry DMSO (5 mL) was vigorously stirred for 9 h at 140 °C. After cooling to room temperature, the reaction mixture was added into water, and then extracted with CHCl<sub>3</sub>. The combined organic layers were washed with water, and dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl<sub>3</sub>), and dried under vacuum to give CzTPN as a yellow solid (yield = 0.53 g, 23%). This compound was further purified by temperature-gradient sublimation before use. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.23 (s, 2H), 8.20 (d, *J* = 7.8 Hz, 4H), 7.54 (td, *J* = 7.8 and 1.2 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H). Anal. calcd (%) for C<sub>32</sub>H<sub>18</sub>N<sub>4</sub>: C 83.82, H 3.96, N 12.22; found: C 83.75, H 3.89, N 12.16.

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**Fig. S1.** <sup>1</sup>H NMR spectrum of PzCz in CDCl<sub>3</sub>. The inset shows the magnified view. The peak with \* denotes the resonance from CHCl<sub>3</sub>.



Fig. S2. MALDI-TOF mass spectrum of PzCz. The inset shows the magnified view.



Fig. S3. TGA thermogram of PzCz under N<sub>2</sub>.



Fig. S4. AFM image of a pure PzCz thin film on an ITO-coated glass substrate.



Fig. S5. Photoelectron yield spectrum of a pure PzCz thin film.



**Fig. S6.** Frontier orbital distributions of CzTPN calculated at the B3LYP/6-31G(d) level. The calculated HOMO and LUMO energies are -5.79 eV and -2.70 eV, respectively. The singlet and triplet excited energies are calculated to be 2.48 eV and 2.29 eV, respectively, resulting in a calculated  $\Delta E_{ST}$  of 0.19 eV.



**Fig. S7.** Fluorescence and low-temperature phosphorescence spectra of a CzTPN:mCP codeposited film.



**Fig. S8.** (a) Current density–voltage–luminance (*J–V–L*) curves and (b) external EL quantum efficiency for a green TADF-OLED (Device III) with the configuration of ITO/ $\alpha$ -NPD (35 nm)/mCP (10 nm)/3 wt%-4CzIPN:PzCz (20 nm)/PPT (40 nm)/LiF (0.8 nm)/Al (80 nm). The inset represents the EL spectrum taken at 10 mA cm<sup>-2</sup>.



**Fig. S9.** *J*–*V* curves for electron-only devices with the structure of ITO/PPT (20 nm)/PzCz or mCP (60 nm)/PPT (20 nm)/LiF (0.8 nm)/Al (80 nm) and ITO/3 wt%-CzTPN:PzCz (60 nm)/PPT (20 nm)/LiF (0.8 nm)/Al (80 nm).