Supporting Information

Selectively Modulating Triplet Exciton Formation in Host Materials for Highly Efficient Blue Electrophosphorescence

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1. Materials and synthesis

Materials: The manipulations involving air-sensitive reagents were performed in an atmosphere of dry N_2 . The chemicals and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich or Acros, and used without further purification. Tetrahydrofuran (THF) was dried and purified by routine procedures.

Characterization methods: ¹H and ¹³C-nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shied Plus 400 MHz instrument with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. The quoted chemical shifts are in *ppm* and the *J* values are expressed in Hz. The splitting patterns have been designed as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet). The MALDI-TOF-MS was determined on a Buker Daltonics flex Analysis. High resolution mass spectra were recorded on a LCT Premier XE (Waters) HRMS spectrometry. Element analysis was performed on a Elementar Vario EL III elemenal analyzer.

Synthesis



Scheme S1. The synthetic route of the host materials.

The synthesis of 9-(4-(triphenylsilyl)phenyl)-9H-carbazole (SiPCz)

To a solution of 1,4-dibromobenzene (2.36 g, 10 mmol) in freshly distilled THF (30 mL) was added a solution of *n*-butyllithium (*n*-BuLi, 2.5 M in *n*-hexane, 4.2 mL, 10.5 mmol) dropwise at -78°C. After the reaction mixture was stirred for 2 h, chlorotriphenylsilane (2.95 g, 10 mmol) dissolved in freshly distilled THF was added into in one portion. The reaction was allowed to warm to room temperature and stirred overnight. Then, the reaction was quenched with water (50 mL) and extracted with dichoromethane (CH₂Cl₂, 3×100 mL) for three times. The combined organic layers were collected, dried over anhydrous sodium sulphate (Na₂SO₄), filtered and evaporated to remove the solvent. The crude solid product of (4-bromophenyl)triphenylsilane was further purified by flash column chromatography on silica gel (300-400 mesh). Yield: 3.36 g of white solid (81%). ¹H NMR (400 MHz, CDCl₃, *ppm*): δ 7.39 (m, 7H), 7.44 (m, 4H), 7.51 (s, 1H), 7.54 (m, 7H); ¹³C NMR (100 MHz, CDCl₃, *ppm*) 124.75, 128.03, 129.82, 131.11, 133.30, 133.62, 135.83, 136.33, 137.94.

A mixture of (4-bromophenyl)triphenylsilane (2.49 g, 6 mmol), carbazole (2.51 g, 15 mmol), Cu-bronze (0.17 g, 2.64 mmol), potassium carbonate (3.35 g, 24.24 mmol) in dry nitrobenzene (30 mL) was stirred and refluxed under N₂ atmosphere for 24 h. After the evaporation of the solvent, distilled water (50 mL) was added into and the reaction mixture was extracted with CH₂Cl₂ for three times (3×100 mL). The combined organic layers were collected, dried over Na₂SO₄, filtered and evaporated to remove the solvent. The crude solid product was further purified by flash column chromatography on silica gel (300-400 mesh). Recrystallize several times from ethanol or CH₂Cl₂/hexane to afford the pure compounds of 9- (4-(triphenylsilyl)phenyl)-9H-carbazole (**SiPCz**). Yield: 2.56 g of white solid (85%). ¹H NMR (400 MHz, CDCl₃, *ppm*): δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.46 (m, 13H), 7.61 (d, *J* = 8 Hz, 2H), 7.65 (d, *J* = 6.4 Hz, 6H), 7.82 (d, *J* = 8 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, *ppm*) 109.92, 120.07, 120.32, 123.52, 125.95, 126.15, 128.05, 129.83, 133.89, 135.20,

136.44, 137.89, 139.00, 140.60. HRMS (EI): m/z calcd for $C_{36}H_{27}NSi$ [M+H]⁺: 502.1991; found: 502.1998. Anal. calcd for $C_{36}H_{27}NSi$: C 86.19, H 5.42, N 2.79; found: C 86.27, H 5.37, N 3.03.



Figure S1. ¹H NMR spectrum of 9-(4-(triphenylsilyl)phenyl)-9H-carbazole (SiPCz).



Figure S2. ¹³C NMR spectrum of 9-(4-(triphenylsilyl)phenyl)-9H-carbazole (SiPCz).



Figure S3. HRMS spectrum of 9-(4-(triphenylsilyl)phenyl)-9H-carbazole (SiPCz).

The synthesis of 3,6-dibromo-9-(4-(triphenylsilyl)phenyl)-9H-carbazole

N-Bromosuccinimide (NBS) (0.45 g, 2.5 mmol) was added in small portions to a solution of 9-(4-(triphenylsilyl)phenyl)-9H-carbazole (0.5 g, 1 mmol) in dimethyl formamide (DMF, 20 mL) at 0°C. After being stirred overnight at room temperature, the reaction mixture was poured into water (200 mL) and extracted with CH₂Cl₂. The combined organic layers were collected, dried over Na₂SO₄, filtered and evaporated to remove the solvent. The crude solid product was purified by flash column chromatography on silica gel (300-400 mesh). Yield: 0.50 g of yellow solid (76%). ¹H NMR (400 MHz, CDCl₃, *ppm*): δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.46 (m, 13H), 7.63 (d, *J* = 7.2 Hz, 6H), 7.81 (d, *J* = 8.0 Hz, 2H), 8.20 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, *ppm*) 111.67, 113.22, 123.25, 124.11, 125.95, 128.10, 129.40, 129.92, 133.64, 134.70, 136.11, 138.07, 138.09, 139.56.



Figure S4. ¹H NMR spectrum of 3,6-dibromo-9-(4-(triphenylsilyl)phenyl)-9H-carbazole



Figure S5. ¹³C NMR spectrum of 3,6-dibromo-9-(4-(triphenylsilyl)phenyl)-9H-carbazole

The synthesis of 9'-(4-(triphenylsilyl)phenyl)-9'H-9,3':6',9''-tercarbazole (SiPTCz)

A mixture of 3,6-dibromo-9-(4-(triphenylsilyl)phenyl)-9H-carbazole (0.66 g, 1 mmol), carbazole (0.42 g, 2.5 mmol), Cu-bronze (0.026 g, 0.404 mmol), potassium carbonate (0.56 g, 4.04 mmol) and dry nitrobenzene (PhNO₂, 15 mL) was stirred and refluxed under N₂ atmosphere for 24 h. After remove of the solvent, distilled water (30 mL) was added into and the reaction mixture was extracted with CH₂Cl₂ (3×50 mL). The combined organic layers were collected, dried over Na₂SO₄, filtered and evaporated to remove the solvent. The crude solid product was further purified by flash column chromatography on silica gel (300-400 mesh). Yield: 0.71 g of white solid (85%). ¹H NMR (400 MHz, CDCl₃, *ppm*): δ 7.29 (m, 4H), 7.40 (d, *J* = 4.0 Hz, 8H), 7.47 (m, 9H), 7.64 (dd, *J* = 2.0 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 6H), 7.77 (m, 4H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 7.6 Hz, 4H) , 8.29 (d, *J* = 1.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, *ppm*) 109.71, 111.47, 119.72, 120.32, 123.18, 124.13, 125.92, 126.26, 128.13, 129.96, 130.51, 133.69, 134.86, 136.46, 138.24, 138.40, 140.43, 141.76. MALDI-TOF-MS (m/z) calcd for C₆₀H₄₁N₃Si, exact mass: 831.30 [M]; found: *m/z* 831.10. HRMS (EI): [M+H]⁺: 832.3148; found: 832.3150. Anal. calcd for C₆₀H₄₁N₃Si: C 86.61, H 4.97, N 5.05; found: C 85.75, H 5.13, N 5.14.



Figure S6. ¹H NMR spectrum of 9'-(4-(triphenylsilyl)phenyl)-9'H-9,3':6',9"-tercarbazole

(SiPTCz). 7



Figure S7. ¹³C NMR spectrum of 9'-(4-(triphenylsilyl)phenyl)-9'H-9,3':6',9"-tercarbazole (SiPTCz).



Figure S8. HRMS spectrum of 9'-(4-(triphenylsilyl)phenyl)-9'H-9,3':6',9"-

tercarbazole (SiPTCz).

Table S1. The element analysis of SiPCz and SiPTCz.

Compound	N (%)	C (%)	H (%)
SiPCz	3.03/2.79	86.27/86.19	5.37/5.42
SiPTCz	5.14/5.05	85.75/86.61	5.13/4.97

^aIn the order of experimental and theoretical contents.

2. Measurements

Atom force microscopy: Atomic force microscopy (AFM) measurements were carried out at room temperature using a Bruker Dimension Icon AFM equipped with Scanasyst-Air peak force tapping mode AFM tips from Bruker. The thin films were prepared through vacuum-deposition on indium tin oxides (ITO) substrates under the identical conditions as that in PhOLED device fabrication. Uniform films of **SiPCz** and **SiPTCz** on ITO surface were observed in AFM images with root mean square (RMS) roughness of 2.78 and 3.31 nm, respectively.



Figure S9. The AFM height images $(5 \times 5 \ \mu m^2)$ of vacuum-deposited (a) **SiPCz** and (b) **SiPTCz** films (100 nm in thick) on ITO substrates. The bottom images show the corresponding surface height along the lines in the AFM images.

Solubility test: The solubility of **SiPCz** and **SiPTCz** in different organic solvents of CH_2Cl_2 , $CHCl_3$, tetrahydrofuran (THF), toluene, and chlorobenzene was measured at room temperature.

Compound	CH_2Cl_2	CHCl ₃	THF	Toluene	Chlorobenzene
SiPCz	32	20	21	14	11
SiPTCz	33	25	26	20	17

Table S2. The solubility test of **SiPCz** and **SiPTCz** (in mg mL⁻¹).

Thermal properties: Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to investigate the thermal properties of the compounds. TGA were conducted on a Shimadzu DTG-60H thermogravimetric analyses at a heating rate of 10°C min⁻¹ and a nitrogen flow rate of 50 cm³ min⁻¹. DSC analyses were performed on a Shimadzu DSC-60A instrument under a heating rate of 10°C min⁻¹ and a nitrogen flow rate of 20 cm³ min⁻¹. Compared to **SiPCz**, **SiPTCz** has better thermal properties with higher decomposition temperature (*T*_d) and melting temperature (*T*_m).



Figure S10. DSC traces of (a) SiPCz and (b) SiPTCz at a rate of 10° C min⁻¹ under N₂ atmospher. Shown are from top to bottom: the first heating, second heating, first cooling and second cooling traces.

Photophysical properties: Ultraviolet-visible (UV-Vis) spectra were recorded on an UV-3600 SHIMADZU UV-VIS-NIR spectrophotometer, while fluorescence spectra were obtained using an RF-5301PC spectrofluorophotometer with a Xenon lamp as light source. The phosphorescence spectra of the compounds in CH₂Cl₂ were measured using a time-resolved Edinburgh LFS920 fluorescence spectrophotometer at 77 K, with a 5 ms delay time after the excitation (λ =337 nm) using a microsecond flash lamp. The concentrations of the compound solutions (in CH₂Cl₂) were adjusted to be at about 1×10⁻⁵ mol L⁻¹. The thin solid films made for optical property measurements were prepared by casting solution of the compounds on quartz substrates.

The photoluminescence quantum yields (PLQY) of the compounds in both CH_2Cl_2 solutions (1×10⁻⁵ mol L⁻¹) and thin solid films were measured on an Edinburgh FLSP920 fluorescence spectrophotometer equipped with a Xenon arc lamp (Xe900) and an integrating sphere. The luminescence decay curves were measured also using the time-resolved Edinburgh FLSP920 fluorescence spectrophotometer equipped with a nanosecond hydrogen flash-lamp (nF920). The lifetimes (τ) of the luminescence were obtained by fitting the decay curves with a multi-exponential decay function of

where A_i and τ_i represent amplitude and lifetime, respectively.



Figure S11. PL spectra of the thin films of **SiPCz** and **SiPTCz** doped with various weight contents (1 and 15 wt %) of FIrpic when excited at 300 nm.

Electrochemical properties: Cyclic voltammogram (CV) measurements were performed at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag⁺, referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt wire) in an acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) at a sweeping rate of 100 mV s⁻¹. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO} and E_{LUMO}) of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum) according to the Equations 2 and 3:

$$E_{HOMO} = -\left[E_{onset}^{Ox} - (0.04)\right] - 4.8 \, eV \qquad2$$
$$E_{LUMO} = -\left[E_{onset}^{\text{Red}} - (0.04)\right] - 4.8 \, eV \qquad3$$

where the value of 0.04 V is the onset oxidative voltage of FOC vs Ag/Ag⁺ and E_{onset}^{Ox} and E_{onset}^{Red} are the onset potentials of the oxidation and reduction, respectively.

3. DFT calculations

Theoretical calculations were performed on Gaussian 09 program with the Becke's threeparameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6-31G (d) basis sets.¹ The geometry optimization of transition metal complex was carried out using the standard double- ζ basis sets (LANL2DZ) and effective core potentials (ECPs) for the heavy elements of iridium and B3LYP 6-31g(d) for other atoms.² The geometries at the ground state (S_0) and the lowest triplet excited state (T_1) were fully optimized by spin-restricted and spin-unrestricted DFT calculations respectively at the B3LYP/6-31G (d) level. The optimized geometry at the lowest singlet excited state (S_1) was obtained by TD-DFT calculations at the same functional and basis set. Vibrational frequency calculations were subsequently carried out to confirm that all these optimized structures are corresponding to the minima on the potential energy surfaces. Since the excited states were contributed from combined transitions of frontier orbitals suggested by TD-DFT, to get further insights into the nature of the T_1 and S_1 states, natural transition orbital (NTO) analysis was performed using TD-B3LYP/6-31G (d) at the optimized S_1 and T_1 state geometries. An index (q) named charge-transfer (CT) amount defining the degree of charge separation in donor-acceptor molecules proposed by Adachi and co-workers³ was adopted here to assess the extent of intramolecular charge separation at not only S₀ state, but also S₁, T₁, cationic, and anionic states. The electron density changes upon excitation from S_0 to S_1 or T_1 were also carried out using Multiwfn⁴ based on TD-DFT calculation at the optimized S₀ geometries.

The charge injection, transport and their balance are crucial for optoelectronic devices; therefore, it is important to investigate the ionization potentials (IPs), hole extraction potentials (HEPs), electronic affinities (EAs), electron extraction potentials (EEPs) and reorganization energies (λ) of optoelectronic molecules to evaluate the energy barrier for injection and transport rates of the holes and electrons.⁵ The charge (hole and electron) mobility of **SiPCz** and **SiPTCz** were assessed using the incoherent hopping model, which assumes a charge transport process between two adjacent reactions M[±] + M \rightarrow M + M[±] where M is the neutral molecule interacting with neighboring oxidized or reduced M[±]. The hopping rates of charge transfer can be described by the Marcus–Hush equation:

$$K_{\rm h/e} = \left(\frac{\pi}{\lambda_{\rm h/e}kT}\right)^{1/2} \frac{V_{\rm h/e}^2}{\hbar} \exp\left(-\frac{\lambda_{\rm h/e}}{4kT}\right) \dots 4$$

where $V_{h/e}$ is the electronic coupling matrix element between neighboring molecules; *T* is the temperature; *k* and \hbar refer to the Boltzmann and Planck constants, respectively; $\lambda_{h/e}$ is the hole/electron reorganization energy calculated by the following equations:

$\lambda_{\rm h} = \lambda_+ + \lambda_1$	5
$\lambda_{\rm e} = \lambda_{\rm e} + \lambda_2$	6
$\lambda_{+} = E^{+}(M) - E^{+}(M^{+})$	7
$\lambda_1 = E(\mathbf{M}^+) - E(\mathbf{M}) \dots$	8
$\lambda_{-} = E^{-}(\mathbf{M}) - E^{-}(\mathbf{M}^{-}) \dots$	9
$\lambda_2 = E(\mathbf{M}^{-}) - E(\mathbf{M}) \dots$	10

The singlet and triplet exciton formation possibilities and their ratio of host materials are important during the operation of PhOLEDs. The singlet (χ_S) and triplet (χ_T) exciton generation fractions can be described in the Equations 11, 12 and 13⁵:

$\chi_{S} = \frac{\sigma_{S}}{\sigma_{S} + 3\sigma_{T}} \dots$	11
$\chi_T = \frac{3\sigma_T}{\sigma_S + 3\sigma_T} \dots$	12
$\frac{\sigma_s}{\sigma_T} = \frac{E_{bT}}{E_{bS}} \dots$	

where $\sigma_{\rm S}$ and $\sigma_{\rm T}$ represent the formation cross sections of singlet and triplet excitons and $E_{\rm bS}$ and $E_{\rm bT}$ are the binding energies of the singlet and triplet excitons, respectively.

 $E_{\rm bS}$ and $E_{\rm bT}$ can be calculated as

where E_g is the HOMO-LUMO energy gap. E_{S1} and E_{T1} are excitation energies from the ground state to the lowest excited singlet state (S₁) and the lowest excited triplet state (T₁), respectively.

Table S3. The computational HOMO and LUMO energy levels, energy gap (Eg), singlet (ES1) and triplet (E_{T1}) excitation energies, singlet (E_{bS}) and triplet (E_{bT}) electron-hole binding energies, singlet exciton generation fractions (χ_S) and triplet exciton generation fractions (χ_T) of **SiPCz** and **SiPTCz**.

Comp	B3LYP (eV)		$^{cal}E_{T1}$	$^{cal}E_{S1}$	Binding Energy (eV)		(0/2)	(0/2)	
comp.	НОМО	LUMO	E_{g}	(eV)	(eV)	$^{cal}E_{bS}$	$^{cal}E_{bT}$	$-\chi_{S}(70)$	ΧΤ(70)
SiPCz	-5.32	-0.76	4.56	3.18	3.96	0.60	1.38	43.40	56.60
SiPTCz	-5.16	-1.18	3.98	3.06	3.43	0.55	0.92	35.80	64.20

Table S4. The ionization potential (IP), hole extraction potential (HEP), electronic affinity (EA), electron extraction potential (EEP), relaxation energies (λ_+ , λ_1 , λ_- and λ_2) and reorganization energies (λ_{hole} and $\lambda_{electron}$) of **SiPCz** and **SiPTCz** calculated by B3LYP/6-31G (d) (in eV).

Comp.	IP	HEP	EA	EEP	λ_+	λ_1	λ_	λ_2	$\lambda_{ m hole}$	$\lambda_{ m electron}$
SiPCz	6.72	6.56	-0.35	0.19	0.08	0.07	0.07	0.09	0.15	0.16
SiPTCz	6.05	5.96	-0.07	0.23	0.10	0.09	0.07	0.08	0.19	0.16



Figure S12. Natural transition orbitals (NTOs) describing the optimized molecular structures at (a) the first singlet (S₁) excited state and (b) the lowest triplet (T₁) excited state of the host materials of **SiPCz** and **SiPTCz**. The orbitals on the top correspond to the hole wave functions, while those at the bottom to the electron wave functions (isosurface value = 0.020 *au*).

Table S5. The B3LYP/6-31G (d) calculated reorganization energies of singlet $(\lambda_{+}^{S} \text{ and } \lambda_{-}^{S})$ and triplet $(\lambda_{+}^{T} \text{ and } \lambda_{-}^{T})$ excitons generated by recombination of cationic and anionic polarons of **SiPCz** and **SiPTCz** (in eV).

Comp.		λ_1	λ_2	λ_3	λ_4	λ_{+}^{T}	λ_{-}^{T}	λ_{+}^{S}	λ_ ^s
S:DC-	T_1	0.07	0.09	0.36	0.41	0.46	0.48	-	-
SIFCZ	\mathbf{S}_1	0.07	0.09	0.13	0.01	-	-	0.22	0.08
S:DTC-	T_1	0.09	0.08	0.15	0.19	0.23	0.28	-	-
SIFTCZ	\mathbf{S}_1	0.09	0.08	0.18	0.08	-	-	0.27	0.17

4. Device fabrication and measurements

Typically, ITO-coated glass substrates were etched, patterned, and washed by ultrasonic with detergent, deionized water, acetone, and ethanol in turn. Organic layers were deposited by high-vacuum (10^{-6} Torr) thermal evaporation at a rate of 0.1-0.2 nm s⁻¹. To reduce ohmic loss, a heavily *p*-doped layer of MoO_x (because of the low doping efficiencies of transition-

metal-oxide-based acceptors in amorphous organic matrixes) was directly deposited onto the ITO substrate. The devices were measured after fabrication without encapsulation under ambient atmosphere at room temperature. The layer thickness and the deposition rate (1~2 Å/s) were monitored *in situ* by an oscillating quartz thickness monitor. Electroluminescent (EL) spectra of the devices were measured by JY SPEX CCD3000 spectrometer. The luminance-voltage and current-voltage characteristics were measured simultaneously with a programmable Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. And the external quantum efficiency (EQE) was calculated by the following equation:

$$EQE = \frac{\pi e \eta_{cd/A} \int \lambda p(\lambda) d\lambda}{hcK_m \int p(\lambda) \Phi(\lambda) d\lambda} \dots 16$$

where $\eta_{cd/A}$ is the current efficiency (cd A⁻¹); *h* is the Planck constant; c is the speed of light in vacuum; λ is the wavelength (nm); e is the electron charge; $p(\lambda)$ is the electroluminescent intensity; $\Phi(\lambda)$ is the luminous efficiency; $K_{\rm m}$ is a constant of 683 lm/W.



Figure S13: *J/V* characteristics of the nominal single-carrier transporting devices base on **SiPCz**, and **SiPTCz** (open symbols are for hole-only devices of ITO/MoO_x (5 nm)/NPB (70 nm) /TCTA (5 nm)/host (10 nm)/TCTA (5 nm) /NPB (70 nm)/MoO_x (5 nm)/Al, while the closed symbols for electron-only devices of ITO/Cs₂CO₃ (2 nm)/TmPyPB (35 nm)/host (10 nm) /TmPyPB (35 nm)/Cs₂CO₃(2 nm)/Al).



Figure S14: The normalized electroluminescent spectra of the blue PhOLED devices (ITO/MoO_x/NPB/TCTA/host:FIrpic/TmPyPB/Cs₂CO₃/Al) using host materials of (a) **SiPCz** and (b) **SiPTCz** at various driving voltages with the corresponding Commission Internationale de l'Eclairage (CIE) coordinates.

When considering quenching effects of the triplet excitons, the EQE of a PhOLED device can be expressed as⁶

where η is the measured EQE, η_0 is the ideal EQE without quenching effects, and the parameter *k* is reduction coefficients of quenching effects, mainly including triplet-triplet annihilation (TTA) and triplet exciton polaron quenching (TPQ).

According to the close triplet energy and frontier orbital energy level of the two host materials, η_0 for **SiPCz** and **SiPTCz** can be approximately equal. Thus, relative reduction ratio of quenching effects can be estimated by comparison on $\sum k$ according to Equation 17 as:

where subscript A and B refer to two different devices using SiPCz and SiPTCz as the host materials, respectively.

In this way, if $\eta_0 = 30\%$ is the theoretical extreme for conventional PhOLEDs, $\sum k$ ratio between **SiPCz** and **SiPTCz** is 0.59, corresponding to a large relative triplet-involved quenching reduction ratio up to 41%.

In order to experimentally measure the hole and electron mobilities of SiPCz and SiPTCz films, space charge limited current (SCLC) model was applied on the hole-only and electron-only devices of ITO/MoO_x (5 nm)/host (100 nm)/MoO_x (5 nm)/Al and ITO/LiF (1 nm)/host (50 nm)/LiF (1 nm)/Al, respectively. The current density (*J*) in these devices follows the field-dependent space charge limited current (SCLC) model of Mott-Gurney,^[8] which is given as:

where V is electrical voltage, d is film thickness, μ_0 is the average mobility, ε_0 is the permittivity of free space (8.854×10⁻¹² F m⁻¹), and ε is dielectric constant of the film. By fitting the experimental J/V curves with Equation 19, the hole mobilities of **SiPCz** and **SiPTCz** are measured to be 1.40×10⁻⁷ and 1.11×10⁻⁵ cm² V⁻¹ s⁻¹ respectively, while their electron mobilities are 9.54×10⁻⁸ and 2.86×10⁻⁷ cm² V⁻¹ s⁻¹ (**Figure S15**).



Figure S15: *J/V* characteristics of the (a) hole-only and (b) electron-only devices of **SiPCz** and **SiPTCz** with the device structure of ITO/MoO₃ (5 nm)/host (100 nm)/MoO₃ (5 nm)/Al and ITO/LiF (1 nm)/host (50 nm)/LiF (1 nm)/Al, respectively. Symbols show the experimental data, while lines are the fitting curves according to field-dependent SCLC model to deduce their charge mobilities.

To experimentally verify the higher singlet exciton generation ratio of **SiPCz** than that of **SiPTCz** in PhOLED devices, we fabricated FIrpic-free OLED devices with the identical device structures of the corresponding PhOLED devices. The fluorescent OLEDs using **SiPCz** as emitting layers (10 nm) with the same device configuration as their PhOLEDs achieved the maximum efficiencies as 0.77 cd A⁻¹ for CE, 0.44 lm W⁻¹ for PE, and 0.72% for EQE, which are much higher compared to that based on **SiPTCz** with 0.18 cd A⁻¹ for CE,

0.09 lm W⁻¹ for PE, and 0.20% for EQE (Table S6). From the device performance of the fluorescent OLEDs, the singlet exciton recombination efficiency (η_s) can be derived as⁷

where Φ_{EL} is EQE of the OLED device, Φ_{PL} is PLQY of the emitting solid in thin film, η_{oc} is out coupling factor which is normally 0.2 for organic solid, γ is exciton recombination efficiency, and χ_S is singlet fraction of excitons generated electronically. The maximum η_S of **SiPCz** and **SiPTCz** based OLEDs were found to be 17.6% and 7.9%, respectively, according to the maximum EQE of the devices. The significantly higher η_S of **SiPCz** confirms the higher singlet exciton formation during the PhOLED operation.

 Table S6. Device performances of the FIrpic-free OLED devices using SiPCz and SiPTCz as fluorescent emitters.

Uost	Turn-on	Maximum Efficiency					
nost	$Voltage^{a}(V)$	$CE (cd A^{-1})$	$PE(Im W^{-1})$	EQE (%)	(%)		
SiPCz	4.0	0.77	0.44	0.72	17.6		
SiPTCz	4.2	0.18	0.09	0.20	7.9		

^{*a*}At 1 cd m⁻²; ^{*b*}The singlet exciton recombination efficiency (η_s) according to equation 20.



Figure S16. Efficiencies-luminance curves of the $Ir(ppy)_3$ -based green PhOLED device. The device structure is ITO/MoO_x (5 nm)/NPB (70 nm)/ TCTA (5 nm)/Host: $Ir(ppy)_3$ (10 nm, 15%) /TmPyPB (35 nm)/Cs₂CO₃ (2 nm)/Al (100 nm).

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