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

Huanhuan Li,[†] Ran Bi,[†] Ting Chen,[†] Kai Yuan,[†] Runfeng Chen,*[,†] Ye Tao,[†] Hongmei Zhang,*[,†] Chao Zheng,[†] and Wei Huang*[,†,‡]

[†]Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials, Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China

[‡]Key Laboratory of Flexible Electronics & Institute of Advanced Materials, Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China

**S** *Supporting Information*

**ABSTRACT:** The concept of limiting the triplet exciton formation to fundamentally alleviate triplet-involved quenching effects is introduced to construct host materials for highly efficient and stable blue phosphorescent organic light-emitting diodes (PhOLEDs). The low triplet exciton formation is realized by small triplet exciton formation fraction and rate with high binding energy and high reorganization energy of triplet exciton. Demonstrated in two analogue molecules in conventional donor–acceptor molecule structure for bipolar charge injection and transport with nearly the same frontier orbital energy levels and triplet excited energies, the new concept host material shows significantly suppressed triplet exciton formation in the host to avoid quenching effects, leading to much improved device efficiencies and stabilities. The low-voltage-driving blue PhOLED devices exhibit maximum efficiencies of 43.7 cd A$^{-1}$ for current efficiency, 32.7 lm W$^{-1}$ for power efficiency, and 20.7% for external quantum efficiency with low roll-off and remarkable relative quenching effect reduction ratio up to 41%. Our fundamental solution for preventing quenching effects of long-lived triplet excitons provides exciting opportunities for fabricating high-performance devices using the advanced host materials with intrinsically small triplet exciton formation cross section.

**KEYWORDS:** *host material, exciton formation cross section, PhOLEDs, singlet and triplet ratio*
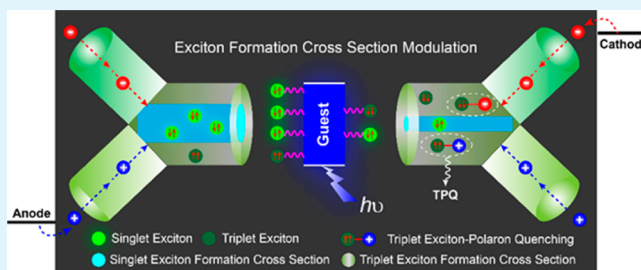
## INTRODUCTION

The ultimate challenge in fabricating high-performance phosphorescent organic light-emitting diodes (PhOLEDs) with high efficiency and stability is to develop ideal host materials capable of confining triplet excitons on the phosphor guest of metal-complex dopants,[1,2] facilitating efficient and balanced hole and electron injection and transporting,[3,4] and suppressing triplet-involved quenching effects, such as triplet–triplet annihilation (TTA), triplet exciton–polaron quenching (TPQ), and electric field induced exciton dissociation of both guest and host molecules.[5–12] Commonly, the confinement of triplet excitons on guest molecules can be realized using host materials with higher triplet energy ($E_T$) than that of the guest (triplet emitter) to promote the exothermic energy transfer from host to guest and prevent back transfer from guest to host;[13,14] the balanced charge injection and transport can be achieved either through device structure optimization using suitable charge transporting layers or through chemical modifications to prepare bipolar host materials using both electron-transporting groups (acceptors) and hole-transporting units (donors).[15,16] However, there are very few reports that

have focused on the alleviation of exciton quenching effects through host molecular structure design.[17,18] Indeed, the doped triplet emitters are almost free of TTA and TPQ effects due to their good dispersion in host and quick radiative deactivation with short lifetime (~microsecond).[19] However, the involvement of host materials in both carrier-transport and -recombination would intrinsically facilitate charge-triplet exciton interactions and aggravate the host-localized TPQ effect. Xu et al.[17,20] recently used a host molecule featured by independent energy transfer and charge transfer channels with separated triplet-state location and charged moieties to realize a remarkable relative TPQ reduction ratio of 30% in red PhOLEDs. However, the extension of this complicated molecular design strategy to blue PhOLEDs is a horrible challenge, since the high triplet energy requirement of the host for blue emitters will easily result in heavy interferences between triplet-state location moieties and carrier-transporting

groups, leading to overlapped energy transfer and charge transfer channels and thus the inevitable quenching effects of the host triplet excitons.

Fundamental insights into the operation mechanism of PhOLEDs (Scheme 1a) may produce alternative solutions.

**Scheme 1. (a) Two Paths for the Excitation of Doped Guest (G) in PhOLEDs and (b) Molecular Structures of the Bipolar Host Materials (H) of SiPCz and SiPTCz[a]**
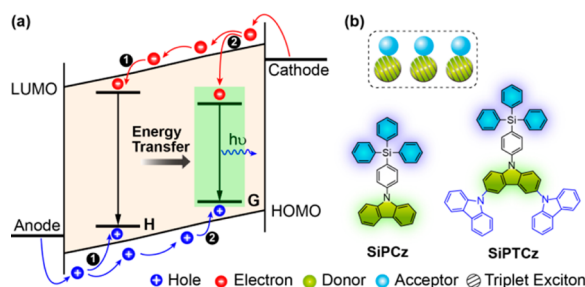


[a]Inset: illustration of host molecular design and triplet-state localization control.

Typically, the doped guests get excited in two ways: (1) energy transfer from host to guest (path 1) and (2) direct charge trapping (path 2).[21] In path 1, the host molecules need to be excited first before the Förster and/or Dexter energy transfer to the guest, but the simultaneous carrier-transport and recombination would result in strong charge−exciton interactions and especially the TPQ effect of the long-lived triplet excitons, leading to heavy roll-off in PhOLED performance especially at high driving voltages.[22] In path 2, host excitons are not produced, and thus, host-localized TTA and TPQ effects are perfectly eliminated; however, direct charge trapping generally needs large energy bandgap ($E_g$) with sufficiently large electron and hole trap depth, which in turn leads to poor conductivity and high operation voltages of the devices.[23] To overcome the dilemma, we reason that TPQ effects can be greatly suppressed when a majority of the excitons produced electronically are at the singlet spin state with short lifetime (∼nanosecond) by controlling the singlet−triplet ratio of exciton formation cross section. When the triplet exciton formation of the host is controlled to be small, the TTA and TPQ processes of the PhOLED devices are largely eliminated, but the efficient and balanced charge injection and transport for device operation and high triplet energy for triplet guest excitons confinement are preserved, providing exciting approaches in host material design for blue PhOLEDs.

Following these understandings on designing new concept host materials with low triplet exciton formation cross section, we prepared a wide-bandgap bipolar host material of 9-(4-(triphenylsilyl)phenyl)-9H-carbazole (SiPCz) containing hole-transporting carbazole, π-conjugation blocker of weak electron-transporting triphenylsilane,[24,25] and phenyl bridge in donor−acceptor molecular structure (Scheme 1b). Its analogue of 9′-(4-(triphenylsilyl)phenyl)-9′H-9,3′:6′,9″-tercarbazole (SiPTCz), which contains the same building blocks with normal triplet exciton formation cross section, was also synthesized for comparison. SiPCz shows similar triplet energy and frontier orbital energy levels with similar photophysical and electrochemical properties to those of SiPTCz, but its triplet exciton formation cross section is selectively tuned to be relatively lower as revealed by both theoretical and

experimental investigations. Consequently, a large amount of the SiPCz excitons generated electronically are in singlet spin state, leading to significantly suppressed triplet-involved quenching effects with remarkable reduction ratio of 41% in PhOLEDs, relative to its analogue of SiPTCz. This is highly instructive for rational design of high-performance organic semiconductors with concerns of suppressing exciton quenching effects via the triplet exciton formation cross section control strategy.

## RESULTS AND DISCUSSION

**Synthesis, Solubility, and Thermal Properties.** SiPCz and SiPTCz were conveniently synthesized by Ullmann cross-coupling reactions in high yields (Scheme S1).[26] Structural characterization was established by NMR spectroscopy, elemental analysis, and high-resolution mass spectrometer (HRMS) (Figures S1−S8). With benefit from the large and nonconjugated triphenylsilane group, the excellent solubility in common organic solvents and good abilities in forming uniform and amorphous pinhole-free thin films of the two compounds were identified by solubility test (Table S2) and atom force microscopy (AFM) measurements (Figure S9). Their high thermal stability was also confirmed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure 1 and Figure S10) with decomposition temperature ($T_d$) over 350 °C, glass transition temperature ($T_g$) above 190 °C (SiPTCz), recrystallization temperature ($T_c$) over 145 °C (SiPCz), and melting temperature ($T_m$) around 234 °C (SiPCz) and 350 °C (SiPTCz).
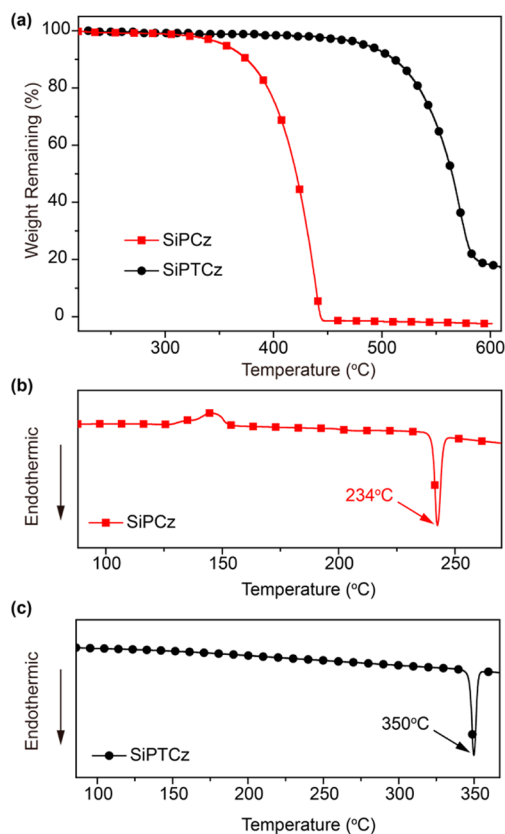


**Figure 1.** (a) TGA and (b and c) DSC curves (second heating) of SiPCz and SiPTCz.

**Optoelectronic Properties.** The photophysical properties of **SiPCz** and **SiPTCz** were investigated by UV−vis absorption and photoluminescence (PL) spectra in both dilute dichloromethane solutions ($1 \times 10^{-5}$ mol L$^{-1}$) and thin solid films (Figure 2 and Table 1). Because of the "insulating" character-
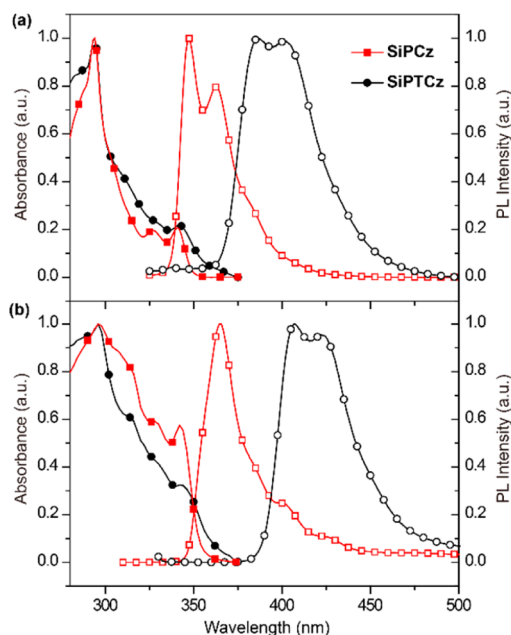


**Figure 2.** Absorption (closed symbols) and photoluminescence (open symbols, excited at 300 nm) spectra of **SiPCz** and **SiPTCz** (a) in dilute ($1 \times 10^{-5}$ mol L$^{-1}$) CH$_2$Cl$_2$ and (b) in thin film.

istic of silane, the electronic communications between conjugated moieties are suppressed, and the absorption spectra of **SiPCz** and **SiPTCz** in solution or in film are similar; they are dominated by the n−$\pi^*$ and $\pi-\pi^*$ transitions of carbazole groups.[27] Also, wide optical bandgaps ($^{opt}E_g > 3.2$ eV) were observed in both **SiPCz** and **SiPTCz** estimated from the onset of their absorption spectra in the solid film. The lower $^{opt}E_g$ of **SiPTCz** is due to the more expanded $\pi$-conjugation of its tricarbazole moiety.[28] The time-resolved PL spectrum studies of the hosts of **SiPCz** and **SiPTCz** show a typical fluorescence emission feature with a lifetime of several nanoseconds (Table 1). However, in contrast to the similar absorption spectra, the two bipolar wide-bandgap molecules show different emission bands. The PL spectra of **SiPTCz** in both solution and film are significantly red-shifted compared to those of **SiPCz**, showing larger Stoke's shifts and enhanced charge transfer (CT) emission, which is in line with its lower PL quantum yield (PLQY) (Table 1). Nevertheless, their PL spectra in the solid film are well-overlapped with the metal-to-ligand charge transfer absorption bands of the widely used blue metal complex of bis[2-(4,6-difluorophenyl)pyridinato-C2,N]-

(picolinato) iridium(III) (FIrpic), enabling efficient Förster and Dexter energy transfer from the host to the blue phosphorescent emitters.[29] Notably, in a composite film containing host and guest molecules, 1 wt % of FIrpic can already lead to efficient energy transfer from host to guest for the dominated FIrpic emission upon photoexcitation (Figure S11).

The frontier orbitals that closely related to the electronic properties were investigated by a combined experimental and theoretical study (Figure 3). Density functional theory (DFT)
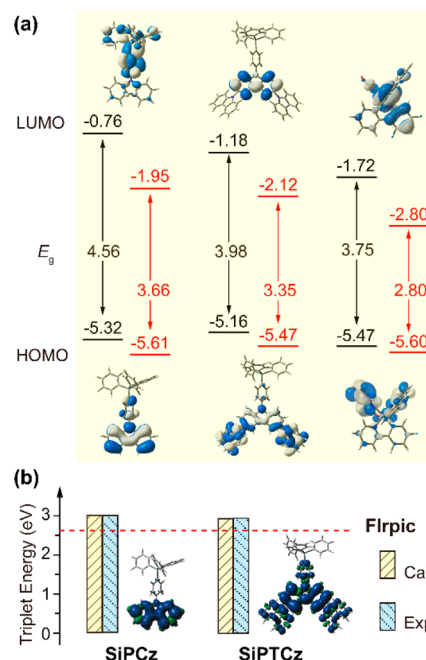


**Figure 3.** (a) DFT calculated (in black) and experimental (in red) HOMO and LUMO energy levels, bandgap ($E_g$) (in eV), (b) the lowest triplet ($T_1$) energies, and contours of the spin density distributions of the $T_1$ states of **SiPCz** and **SiPTCz**.

calculations provided good supports for the electrochemically measured highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO) energy levels and, more importantly, new physical insights.[30] HOMOs determined by the donor of carbazole moieties in **SiPCz** and **SiPTCz** are very close in energy at a high level around −5.5 eV, while LUMOs, although still close in energy around −2.0 eV, are not dominated by the weak acceptor of triphenylsilane in **SiPTCz** but by the carbazole connected to the silane.[28] Possibly, under the combined electron-withdrawing effect of tetraphenylsilane and conjugation effect of adjacent carbazolyls, the central carbazole is enabled with higher electron affinity than triphenylsilane to change the LUMO location from the phenyl bridge and triphenylsilane in **SiPCz** to the central

## Table 1. Photophysical, Electrochemical, and Thermal Properties of SiPCz and SiPTCz

| compd | $T_d^a/T_g/T_m$ (°C) | in CH$_2$Cl$_2$ | | | | $^{opt}E_g{}^b$ (eV) | in film | | | | $^{exp}E_T$ (eV) | $^{cal}E_T$ (eV) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | PLQY | $\tau$ (ns) | | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | PLQY | $\tau$ (ns) | | |
| **SiPCz** | 355/−/234 | 293,327, 343 | 346, 362 | 45.5% | 4.62 | 3.67 | 296, 328, 341 | 365, 402 | 20.5% | 2.47 | 3.01 | 2.98 |
| **SiPTCz** | 485/190/350 | 293, 310, 342 | 387, 402 | 28.1% | 3.70 | 3.26 | 296, 315, 344 | 407, 423 | 12.6% | 3.68 | 2.93 | 2.93 |

$^a$At 5% weight loss. $^b$Estimated from the edge of the absorption spectrum in film.

carbazole in **SiPTCz**. In comparison with the HOMO and LUMO of FIrpic, it seems that direct charge-trapping of the guest can be hardly supported due to the small carrier trap depths especially for the hole-trapping.[31] However, such HOMO and LUMO energy levels are good for charge injection and transport and are convenient in the selection of materials for hole- and electron- transporting layers during PhOLED fabrication.[21]

The triplet energy ($E_T$), which is a key parameter of host materials, was found to be 3.01 and 2.93 eV for **SiPCz** and **SiPTCz**, respectively, deduced from the 0−0 transition peaks of their time-resolved phosphorescence spectra in $CH_2Cl_2$ at 77 K after 5 ms delay (Figure 4). Such an $E_T$ level is close to that of
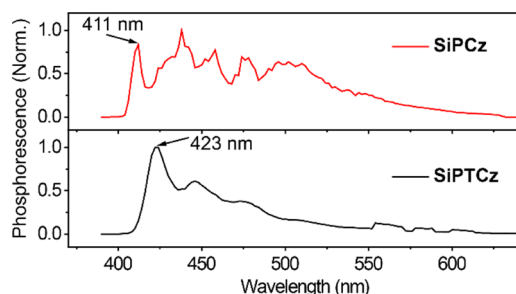


**Figure 4.** Phosphorescence spectra (excited at 337 nm) of **SiPCz** and **SiPTCz** at 77 K in $CH_2Cl_2$.

carbazole (3.05 eV);[32] the modification of carbazole at its 3,6-positions with carbazolyl groups has limited effects on $E_T$ value. The dominating role of carbazole moiety in determining triplet excited state is revealed by DFT calculations that the spin density distribution of the $T_1$ state is mainly localized on the carbazole moieties (Figure 3b). The slight delocalization of the $T_1$ state to adjacent groups in **SiPTCz** leads to slightly lower $E_T$. From the higher $E_T$ of the two hosts than the blue phosphor of FIrpic (2.62 eV),[33] we would expect that (1) the

energy of triplet excitons would be transferred effectively from the host to the guest for the efficient phosphorescent emission and (2) the reversing pathway could be prohibited.

The close HOMO, LUMO, and $E_T$ with small energy variation lower than 0.2 eV between **SiPCz** and **SiPTCz** provide an ideal platform for evaluating effects of frontier orbital distributions at ground states ($S_0$), singlet ($S_1$) and triplet ($T_1$) excited states, and anionic and cationic polaronic states on the exciton generation and transformation in the operation of PhOLEDs. At the optimized $S_1$ and $T_1$ states (Figure 5a,b), the paired and unpaired electron and hole in singlet and triplet excitons have similar distributions that mainly localized on carbazole moieties, demonstrating the central role of carbazole in controlling the excited states. Natural transition orbital (NTO) analysis[34] to consider the whole picture of the electron transitions for the excited states of $S_1$ and $T_1$ also presents the almost identical hole and electron distributions at excited states to the corresponding HOMO and LUMO at $S_1$ and $T_1$ states, supporting the fact that a majority of electron transitions at excited molecular states occur between the HOMO and LUMO of carbazole moieties (Figure S12). However, significantly different moiety participations in **SiPCz** and **SiPTCz** can be distinguished from electron-density distribution change upon $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions based on optimized $S_0$ states (Figure 5c). The large participation of phenyl bridge and triphenylsilane in the $S_0 \rightarrow S_1$ excitation transition of **SiPCz** may be related to a large molecular structure rearrangement at its $S_1$ state with significantly decreased dihedral angle ($\theta$) up to 11°. The structure rearrangements at different molecular states determine kinetically to a large extent the exciton generation and transformation processes.

**Singlet and Triplet Exciton Generation Dynamics.** To study the generation of the singlet and triplet excitons excited electronically in PhOLEDs, the singlet ($\chi_S$) and triplet ($\chi_T$) exciton formation fractions were studied.[35] Experimentally, a
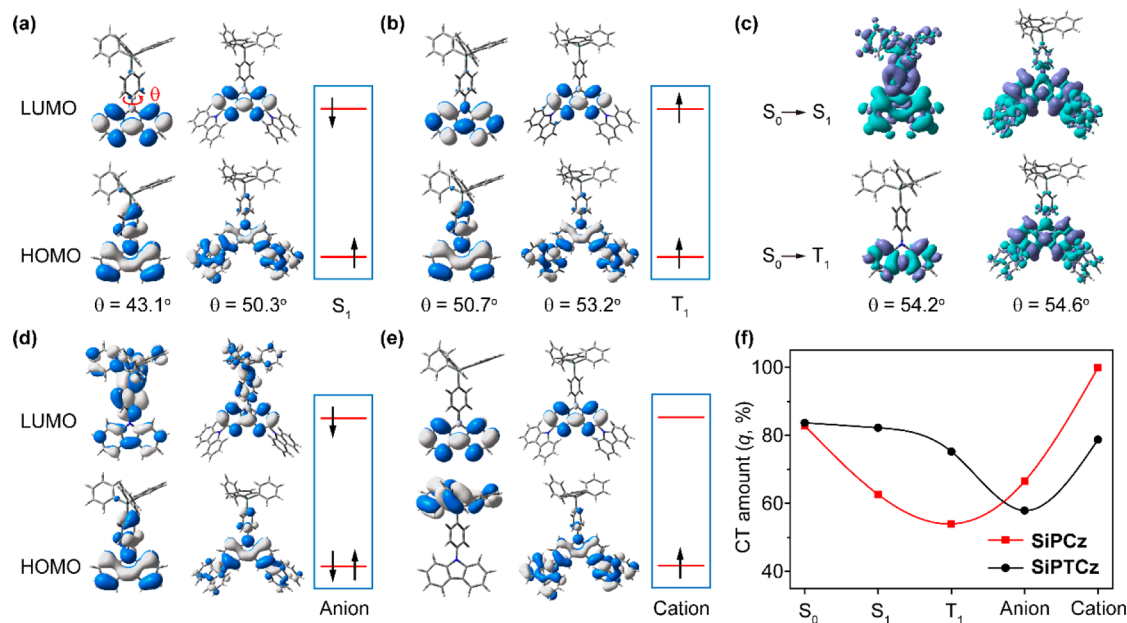


**Figure 5.** DFT calculated HOMO and LUMO distributions at optimized (a) $S_1$, (b) $T_1$, (d) anion, and (e) cation states; (c) change of electron-density distribution upon $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions based on $S_0$ state; and (f) CT amount of molecular structures at $S_0$, $S_1$, $T_1$, cationic, and anionic states of **SiPCz** and **SiPTCz**. Inset shows $\theta$ representing the rotation angle between the phenyl bridge and the carbazole molecular planes.

**Table 2. Experimental HOMO and LUMO Energy Levels, Energy Gap ($E_g$), Singlet ($E_{S1}$) and Triplet ($E_{T1}$) Excitation Energies, Singlet ($E_{bS}$) and Triplet ($E_{bT}$) Binding Energies, and Singlet ($\chi_s$) and Triplet ($\chi_T$) Exciton Generation Fractions of SiPCz and SiPTCz**

| compd | CV (eV) | | | $^{exp}E_{T1}$ (eV) | $^{exp}E_{S1}$ (eV) | binding energy (eV) | | $\chi_S$ (%) | $\chi_T$ (%) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | HOMO | LUMO | $E_g$ | | | $^{exp}E_{bS}$ | $^{exp}E_{bT}$ | | |
| **SiPCz** | −5.61 | −1.95 | 3.66 | 3.00 | 3.40 | 0.26 | 0.66 | 45.84 | 54.16 |
| **SiPTCz** | −5.47 | −2.12 | 3.35 | 2.94 | 3.05 | 0.30 | 0.41 | 31.29 | 68.71 |

much larger triplet binding energy ($E_{bT}$) of **SiPCz** was observed, leading to a much increased $\chi_S$ up to 45.8%, which is significantly higher than the normal ratio (25%)[36] of singlet excitons excited electronically (Table 2). The increase of singlet exciton fraction is highly advisable for efficient long-range Förster energy transfer to alleviate the triplet-involved quenching effects. The computational results support well of the experimental findings with higher $E_{bT}$ and $\chi_S$ of **SiPCz**; therefore, better PhOLED device performance of **SiPCz** can be expected thermodynamically from suppressed generation of triplet exciton with low $\chi_T$.

The exciton generation kinetics upon electronic excitation was also investigated via the frontier orbital distributions at cationic and anionic states (Figure 5d,e). When a hole is injected to the HOMO of an anionic molecule or an electron to the LUMO of a cationic molecule, excitons will be formed.[37] In this sense, the HOMO and LUMO of anionic and cationic molecules intrinsically determine the exciton formation behaviors during the initial stage of electronic excitation. The heavy overlap of HOMO and LUMO distributions facilitates the hole−electron interactions for exciton formation due to the strong electronic coupling, while separately distributed HOMO and LUMO of anionic and cationic molecules are generally not good for the exciton formation due to low binding energy and long separation distance between the injected hole and electron.[38] From Figure 5d, HOMO and LUMO of both **SiPCz** and **SiPTCz** are partially overlapped at the anionic state, suggesting their moderate exciton formation cross sections. However, in the cationic state, HOMO of **SiPCz** is dominated by triphenylsilane instead of the donor of carbazole, probably due to the radical reagent feature of triphenylsilane.[39] Consequently, the almost completely separated HOMO and LUMO distribution of cationic **SiPCz** indicates the almost forbidden exciton formation of the compound via this channel.

In order to give a quantitative description of the HOMO and LUMO overlap extent, the charge transfer (CT) amount ($q$), previously used to assess CT properties upon excitation,[40] was adopted (Figure 5f). A higher $q$ stands for more separated HOMO and LUMO. The typical D−A molecule characteristics of separated HOMO and LUMO with $q$ of 80% were found for both **SiPCz** and **SiPTCz** at the ground state ($S_0$). While at the $S_1$ state, a lower $q$ was observed for **SiPCz**, which may be responsible for its higher photoluminescence quantum yield (PLQY).

We further proposed a new parameter of exciton generation reorganization energy to evaluate the exciton formation kinetics for the first time. Upon the electronic excitation of host molecules in PhOLEDs, the formation of singlet and triplet excitons can be described as follows

$$M^+ + M^- \rightarrow M^{S/T} + M_0 \tag{1}$$

where $M^+$ and $M^-$ are the respective cationic and anionic states of the host molecules, $M^{S/T}$ is the singlet or triplet exciton molecular state, and $M_0$ is the neutral ground molecule state. In

principle, the host molecules get electronically excited when cationic and anionic molecules meet together to form a charge transfer exciton ($M^+/M^-$); from the $M^+/M^-$ pair, the exciton can result either through hole-injection from $M^+$ to $M^-$ or through electron injection from $M^-$ to $M^+$. Thus, the recombination process to produce excitons contains two possible ways: the first one is $M^+ \rightarrow M^{S/T}$ and $M^- \rightarrow M_0$, and the other is $M^- \rightarrow M^{S/T}$ and $M^+ \rightarrow M_0$. To study the generation kinetics of the excitons, the reorganization energy of exciton was defined here as the energy cost due to geometry modifications to go from a charged molecule to an excited molecule and to a neutral molecule. The reorganization energies for exciton generation from cationic state ($M^+$) and anionic state ($M^-$) to the corresponding singlet or triplet exciton ($M^{S/T}$) can be used to assess the relative feasibilities of the two ways for producing singlet and triplet excitons. The lower reorganization energy means the faster generation rate of the exciton. The reorganization energies for the singlet ($\lambda_+^S$) and triplet ($\lambda_+^T$) excitons generated via the first way from $M^+ \rightarrow M^{S/T}$ and $M^- \rightarrow M_0$ and singlet ($\lambda_-^S$) and triplet ($\lambda_-^T$) excitons generated via the second way from $M^- \rightarrow M^{S/T}$ and $M^+ \rightarrow M_0$ were calculated by using eqs 2−5 as demonstrated in Figure 6 and Table S5.

$$\lambda_+^{S/T} = \lambda_2 + \lambda_3 \tag{2}$$

$$\lambda_-^{S/T} = \lambda_1 + \lambda_4 \tag{3}$$

$$\lambda_3 = E^{S/T}(M^+) - E^{S/T}(M^{S/T}) \tag{4}$$

$$\lambda_4 = E^{S/T}(M^-) - E^{S/T}(M^{S/T}) \tag{5}$$

The significantly lower $\lambda_S$ of **SiPCz** in both channels and especially the much lower $\lambda_-^S$ through hole-injection to $M^-$ in producing singlet excitons strongly support the kinetically more facile singlet exciton generation rate (Table S3) of this host material upon electronic excitation.
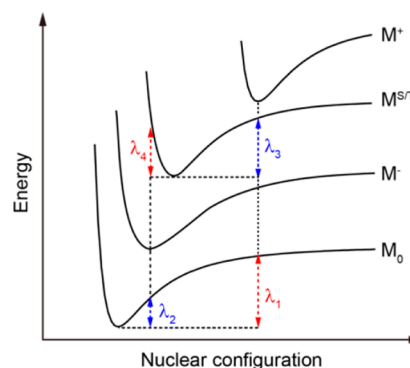


**Figure 6.** Calculation of reorganization energies of singlet and triplet excitons electronically excited in devices.
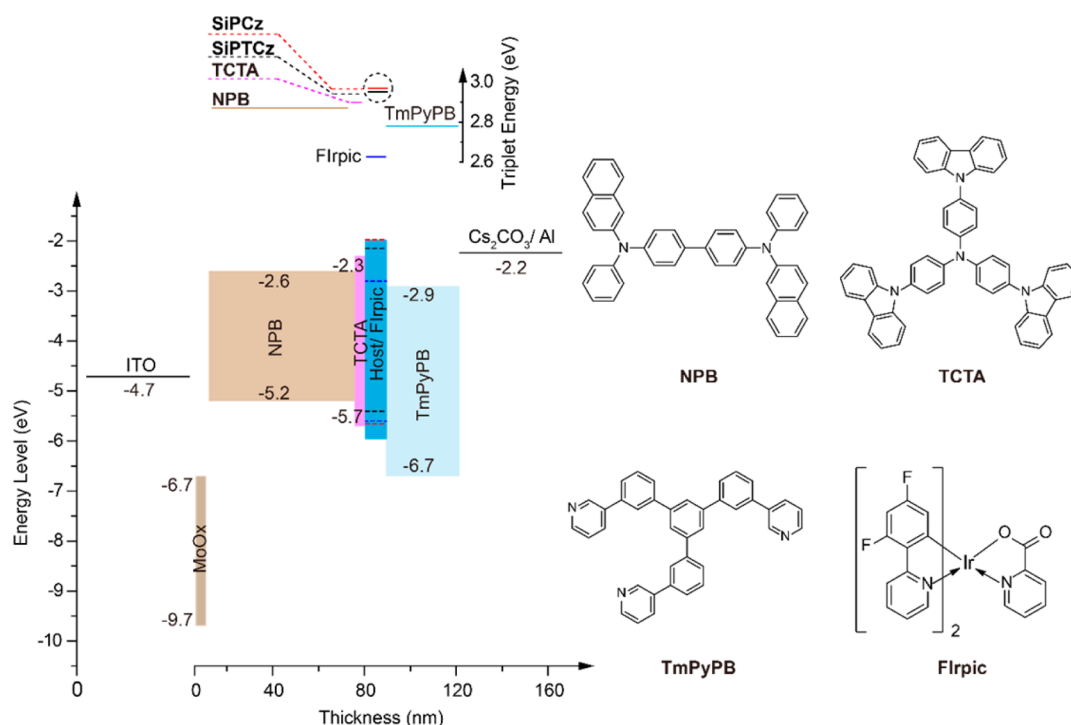
**Figure 7.** Blue PhOLED device configuration and energy level diagram using **SiPCz** and **SiPTCz** as the host materials and FIrpic as the guest material.

**Blue PhOLED Device Properties.** To demonstrate the superiority of the low triplet exciton formation of the new concept host material that benefited from both the low triplet exciton formation fraction and the lower triplet exciton generation rate with alleviated long-lived triplet exciton quenching effects, blue-emitting PhOLED devices of **SiPCz** and **SiPTCz** doped with FIrpic were fabricated in a conventional configuration of ITO/MoO$_x$ (5 nm)/NPB (70 nm)/TCTA (5 nm)/host:FIrpic (10 nm, 15%)/TmPyPB (35 nm)/Cs$_2$CO$_3$ (2 nm)/Al (100 nm) (Figure 7).[41] The bipolar charge transport properties of the host materials were verified by their hole-only and electron-only devices (Figure S13), and DFT calculations of carrier motilities based on the hopping model of Marcus−Hush equation. The small and close reorganization energies of hole and electron transport (Table S4) theoretically support the balanced ambipolar conducting behavior of these two molecules. The current density−voltage−luminance ($J$−$V$−$L$) characteristics of the devices (Figure 8a) show turn-on voltages at as low as 3.1 V and the highest luminescence over 34 800 cd m$^{-2}$. Both PhOLED devices are highly stable in electroluminescence at varying operating voltages with identical emission from the sky-blue emitter of FIrpic (Figure S14), indicating excellent energy transfer and/or charge transfer from host to guest.

In accord with the results of single-carrier-transporting devices and reorganization energy calculations of charge transport, the **SiPTCz**-based PhOLED device exhibited higher current density due to the higher carrier mobilities of **SiPTCz** than that of **SiPCz** via the field-dependent space charge limited current (SCLC) model (Figure S15). The increased current did produce enhanced luminance, but lower efficiencies were observed in the **SiPTCz**-based device with the maximum current efficiency (CE) of 29.1 cd A$^{-1}$, power efficiency (PE) of 22.8 lm W$^{-1}$, and external quantum efficiency (EQE) of 14.2% (Figure 8b). In contrast, the **SiPCz**-hosted device showed
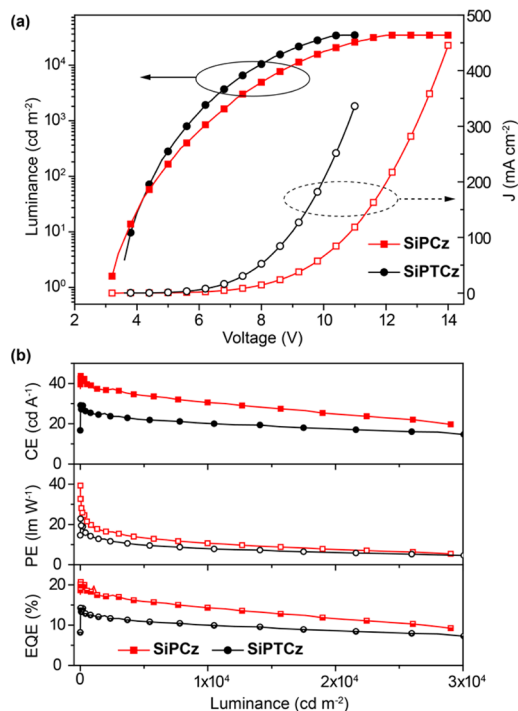


**Figure 8.** (a) Current density ($J$) (open)−luminance (solid)−voltage curves and (b) efficiency−luminance curves of the PhOLED devices.

much improved maximum efficiencies of 43.7 cd A$^{-1}$ for CE, 32.7 lm W$^{-1}$ for PE, and 20.7% for EQE with generally 30% improvement of the device performance compared to that based on **SiPTCz** (Table 3). More importantly, the very low efficiency roll-off of the **SiPCz**-hosted device can be observed, only 5.9% and 6.1% for CE and EQE at 100 cd m$^{-2}$, and 11.2% and 12.1% at 1000 cd m$^{-2}$, respectively. These efficiencies and

**Table 3. Device Performance of Blue PhOLEDs Hosted by SiPCz and SiPTCz**

| compd | opperating voltage[a] (V) | max efficiency[b] | efficiency[c] | | | $q^d$ (%) | $\chi_T{}^e$ (%) | roll-off[c] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | CE | PE | EQE | | | CE | PE | EQE |
| **SiPCz** | 3.1, <4.7, <6.3 | 43.7, 32.7, 20.7 | 41.1, 38.8 | 27.9, 19.5 | 19.4, 18.2 | 66.3/99.9 | 54.2 | 5.9, 11.2 | 14.7, 40.4 | 6.1, 12.1 |
| **SiPTCz** | 3.2, <4.8, <5.8 | 29.1, 22.8, 14.2 | 27.1, 25.0 | 18.5, 13.5 | 13.3, 12.3 | 57.9/78.7 | 68.7 | 6.8, 14.2 | 18.9, 40.8 | 6.4, 13.4 |

[a]In the order of 1, 100, and 1000 cd m$^{-2}$. [b]In the order of CE (cd A$^{-1}$), PE (lm W$^{-1}$), and EQE (%). [c]In the order of 100 and 1000 cd m$^{-2}$. [d]CT amount ($q$) at anionic and cationic states. [e]Triplet exciton formation fraction ($\chi_T$).

efficiency stabilities are among the best results of low-voltage-driving blue PhOLEDs reported to date.[42]

Considering the similar HOMO/LUMO energy levels, close triplet energies, and comparable hole/electron transport of **SiPCz** and **SiPTCz** in the designed device structure, the main reason for the much improved performance of PhOLED devices based on **SiPCz** should be closely related to its low triplet exciton formation characteristic. According to the device configuration (Figure 7), the direct charge trapping of the guest with negligible trap depth (<0.01 eV) and 15 wt % doping level must be very low.[21] Therefore, the main channel for the FIrpic excitation should be the Förster and/or Dexter energy transfer from the host exciton to the guest. Theoretical calculations of $\chi_S$ and $\lambda_S$ strongly suggest both thermodynamically and kinetically suppressed triplet exciton formation during the electronic excitation of **SiPCz**. To experimentally verify the higher singlet exciton generation fraction in **SiPCz**-hosted PhOLEDs, the FIrpic-free OLEDs under the identical device structures of the PhOLEDs were fabricated.[43] The fluorescent OLEDs using **SiPCz** emitting layers (10 nm) 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 than that based on **SiPTCz** with 0.18 cd A$^{-1}$ for CE, 0.09 lm W$^{-1}$ for PE, and 0.20% for EQE (Figure 9 and Table S6). Therefore, the

maximum singlet exciton recombination efficiency ($\eta_S$) of **SiPCz** and **SiPTCz** based fluorescent OLEDs were found to be 17.6% and 7.9%, respectively (eq S20). The significantly higher $\eta_S$ of **SiPCz** supports the higher singlet exciton generation upon the electronic excitation of the PhOLEDs. The positive effects of the higher singlet exciton generation of host molecules on the improved PhOLED performance were further confirmed in the green PhOLEDs (Figure S16).

Taking together, during the operation of the PhOLED hosted by **SiPCz**, a larger fraction of host excitons generated electronically are in singlet spin state due to the high $\chi_S$ and low $\lambda_S$; the short-lived singlet excitons are favorable for efficient long-range Förster energy transfer to relieve the quenching effects of excitons. The high generation ratio of singlet exciton could be the most important factor in affording the high device performance of **SiPCz**. The significantly increased efficiencies and suppressed roll-off of **SiPCz**-hosted PhOLEDs provide direct evidence for the alleviated triplet-involved quenching effects with relative reduction ratio up to 41% by comparing the EQEs of **SiPCz**- and **SiPTCz**-hosted PhOLED devices (eqs S17−S18).

## CONCLUSION

In summary, we have demonstrated an effective strategy in alleviating triplet-involved quenching effects of host materials for blue PhOLEDs via limiting triplet exciton formation by controlling triplet exciton generation fraction of the host molecules. As indicated by the higher triplet exciton binding energy and by the lower reorganization energy of singlet exciton, the lower formation fraction of triplet host excitons during the electronic excitation of PhOLEDs can result. Consequently, without reducing the triplet energy and altering frontier orbital energy levels significantly, new concept host materials can be constructed selectively with capabilities in confining excitons on guests, supporting efficient and balanced charge injection and transport of the device, and suppressing triplet-involved quenching of hosts simultaneously. On the basis of such a host molecule of **SiPCz**, highly efficient and stable blue PhOLEDs were fabricated and found to exhibit maximum efficiencies of 43.7 cd A$^{-1}$ for CE, 32.7 lm W$^{-1}$ for PE, and 20.7% for EQE, which are about 30% improvements compared to that based on its counterpart of **SiPTCz**, owing to effective suppressions of triplet-involved quenching effects of TTA and TPQ. This work not only shows the superiority of organic systems with rich and diversified optical and electrical properties after selective and purposeful tuning, but also illustrates a feasible and fundamental solution to independently alleviate triplet exciton quenching effects of host materials for improved performance of PhOLED devices, which is crucial for the rational development of advanced optoelectronic organic semiconductors.
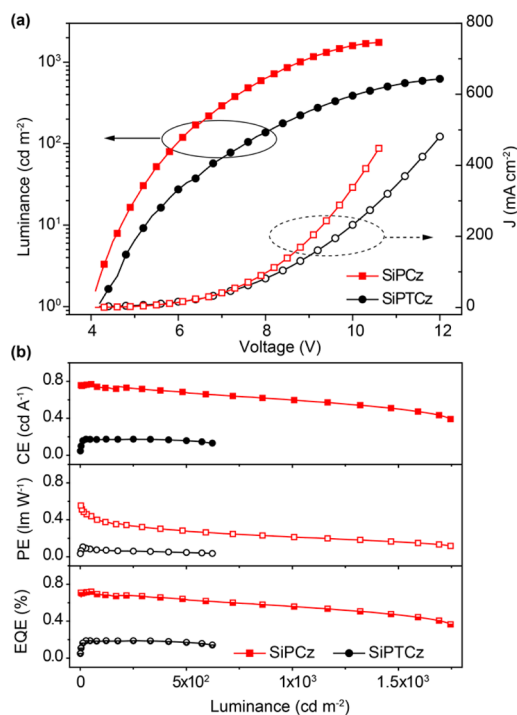


**Figure 9.** (a) Current density ($J$) (open)−luminance (solid)−voltage curves and (b) efficiencies−luminance curves of the FIrpic-free devices.

## ■ AUTHOR INFORMATION

**Corresponding Authors**
*E-mail: iamrfchen@njupt.edu.cn.
*E-mail: iamhmzhang@njupt.edu.cn.
*E-mail: wei-huang@njtech.edu.cn.

**Author Contributions**
H.L. and R.B. contributed equally to this work.

**Notes**
The authors declare no competing financial interest.

## ■ REFERENCES

(1) Zhu, M.; Yang, C. Blue Fluorescent Emitters: Design Tactics and Applications in Organic Light-Emitting Diodes. *Chem. Soc. Rev.* **2013**, *42*, 4963−4976.

(2) Kim, K.; Lee, S.; Moon, C.; Kim, S.; Park, Y.; Lee, J.; Woo Lee, J.; Huh, J.; You, Y.; Kim, J. Phosphorescent Dye-Based Supramolecules for High-Efficiency Organic Light-Emitting Diodes. *Nat. Commun.* **2014**, *5*, 4769−4777.

(3) Han, C.; Zhang, Z.; Xu, H.; Yue, S.; Li, J.; Yan, P.; Deng, Z.; Zhao, Y.; Yan, P.; Liu, S. Short-Axis Substitution Approach Selectively Optimizes Electrical Properties of Dibenzothiophene-Based Phosphine Oxide Hosts. *J. Am. Chem. Soc.* **2012**, *134*, 19179−19188.

(4) Chaskar, A.; Chen, H.; Wong, K. Bipolar Host Materials: A Chemical Approach for Highly Efficient Electrophosphorescent Devices. *Adv. Mater.* **2011**, *23*, 3876−3895.

(5) Reineke, S.; Schwartz, G.; Walzer, K.; Leo, K. Reduced Efficiency Roll-Off in Phosphorescent Organic Light Emitting Diodes by Suppression of Triplet-Triplet Annihilation. *Appl. Phys. Lett.* **2007**, *91*, 123508.

(6) Baldo, M. A.; Adachi, C.; Forrest, S. R. Transient Analysis of Organic Electrophosphorescence. II. Transient Analysis of Triplet-Triplet Annihilation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, 10967−10977.

(7) Zang, F. X.; Sum, T. C.; Huan, A. C. H.; Li, T. L.; Li, W. L.; Zhu, F. Reduced Efficiency Roll-Off in Phosphorescent Organic Light Emitting Diodes at Ultrahigh Current Densities by Suppression of Triplet-Polaron Quenching. *Appl. Phys. Lett.* **2008**, *93*, 023309.

(8) Reineke, S.; Walzer, K.; Leo, K. Triplet-Exciton Quenching in Organic Phosphorescent Light-Emitting Diodes with Ir-Based Emitters. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 125328.

(9) Kalinowski, J.; Stampor, W.; Mężyk, J.; Cocchi, M.; Virgili, D.; Fattori, V.; Di Marco, P. Quenching Effects in Organic Electrophosphorescence. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 235321.

(10) Kan, W.; Zhu, L.; Wei, Y.; Ma, D.; Sun, M.; Wu, Z.; Huang, W.; Xu, H. Phosphine Oxide-Jointed Electron Transporters for the Reduction of Interfacial Quenching in Highly Efficient Blue PHOLEDs. *J. Mater. Chem. C* **2015**, *3*, 5430−5439.

(11) Zhang, Z.; Zhang, Z.; Ding, D.; Wei, Y.; Xu, H.; Jia, J.; Zhao, Y.; Pan, K.; Huang, W. Selectively Investigating Molecular Configuration Effect on Blue Electrophosphorescent Host Performance through a Series of Hydrocarbon Oligomers. *J. Phys. Chem. C* **2014**, *118*, 20559−20570.

(12) Han, C.; Zhu, L.; Zhao, F.; Zhang, Z.; Wang, J.; Deng, Z.; Xu, H.; Li, J.; Ma, D.; Yan, P. Suppressing Triplet State Extension for Highly Efficient Ambipolar Phosphine Oxide Host Materials in Blue PHOLEDs. *Chem. Commun.* **2014**, *50*, 2670−2672.

(13) Lee, C. W.; Lee, J. Y. Above 30% External Quantum Efficiency in Blue Phosphorescent Organic Light-Emitting Diodes Using Pyrido[2,3-b]indole Derivatives as Host Materials. *Adv. Mater.* **2013**, *25*, 5450−5454.

(14) Tao, Y.; Xiao, J.; Zheng, C.; Zhang, Z.; Yan, M.; Chen, R.; Zhou, X.; Li, H.; An, Z.; Wang, Z.; Xu, H.; Huang, W. Dynamically Adaptive Characteristics of Resonance Variation for Selectively Enhancing Electrical Performance of Organic Semiconductors. *Angew. Chem., Int. Ed.* **2013**, *52*, 10491−10495.

(15) May, F.; Al-Helwi, M.; Baumeier, B.; Kowalsky, W.; Fuchs, E.; Lennartz, C.; Andrienko, D. Design Rules for Charge-Transport Efficient Host Materials for Phosphorescent Organic Light-Emitting Diodes. *J. Am. Chem. Soc.* **2012**, *134*, 13818−13822.

(16) Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y. Strategies to Design Bipolar Small Molecules for Oleds: Donor-Acceptor Structure and Non-Donor-Acceptor Structure. *Adv. Mater.* **2011**, *23*, 1137−1144.

(17) Han, C.; Zhu, L.; Li, J.; Zhao, F.; Zhang, Z.; Xu, H.; Deng, Z.; Ma, D.; Yan, P. Highly Efficient Multifluorenyl Host Materials with Unsymmetrical Molecular Configurations and Localized Triplet States for Green and Red Phosphorescent Devices. *Adv. Mater.* **2014**, *26*, 7070−7077.

(18) Han, C.; Zhu, L.; Li, J.; Zhao, F.; Xu, H.; Ma, D.; Yan, P. Rationally Investigating the Influence of T1 Location on Electroluminescence Performance of Aryl Amine Modified Phosphine Oxide Materials. *Chem. - Eur. J.* **2014**, *20*, 16350−16359.

(19) Erickson, N. C.; Holmes, R. J. Engineering Efficiency Roll-Off in Organic Light-Emitting Devices. *Adv. Funct. Mater.* **2014**, *24*, 6074−6080.

(20) Ding, D.; Zhang, Z.; Wei, Y.; Yan, P.; Xu, H. Spatially Optimized Quaternary Phosphine Oxide Host Materials for High-Efficiency Blue Phosphorescence and Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2015**, *3*, 11385−11396.

(21) Tao, Y.; Yang, C.; Qin, J. Organic Host Materials for Phosphorescent Organic Light-Emitting Diodes. *Chem. Soc. Rev.* **2011**, *40*, 2943−2970.

(22) Song, D.; Zhao, S.; Luo, Y.; Aziz, H. Causes of Efficiency Roll-Off in Phosphorescent Organic Light Emitting Devices: Triplet-Triplet Annihilation Versus Triplet-Polaron Quenching. *Appl. Phys. Lett.* **2010**, *97*, 243304.

(23) Park, T. J.; Jeon, W. S.; Park, J. J.; Kim, S. Y.; Lee, Y. K.; Jang, J.; Kwon, J. H.; Pode, R. Efficient Simple Structure Red Phosphorescent Organic Light Emitting Devices with Narrow Band-Gap Fluorescent Host. *Appl. Phys. Lett.* **2008**, *92*, 113308.

(24) Jeon, S. O.; Jang, S. E.; Son, H. S.; Lee, J. Y. External Quantum Efficiency Above 20% in Deep Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* **2011**, *23*, 1436−1441.

(25) Zhang, S.; Xu, Q.; Jing, Y.; Liu, X.; Lu, G.; Liang, X.; Zheng, Y.; Zuo, J. Yellow Electrophosphorescent Devices with Hosts Containing $N^1$-(naphthalen-1-yl)-$N^1$,$N^4$-diphenylnaphthalene-1,4-diamine and tetraphenylsilane units. *RSC Adv.* **2015**, *5*, 27235−27241.

(26) Zhang, S.; Chen, R.; Yin, J.; Liu, F.; Jiang, H.; Shi, N.; An, Z.; Ma, C.; Liu, B.; Huang, W. Tuning the Optoelectronic Properties of 4,4′-N,N′-Dicarbazole-biphenyl through Heteroatom Linkage: New Host Materials for Phosphorescent Organic Light-Emitting Diodes. *Org. Lett.* **2010**, *12*, 3438−3441.

(27) Jiang, W.; Duan, L.; Qiao, J.; Dong, G.; Zhang, D.; Wang, L.; Qiu, Y. High-Triplet-Energy Tri-Carbazole Derivatives as Host

Materials for Efficient Solution-Processed Blue Phosphorescent Devices. *J. Mater. Chem.* **2011**, *21*, 4918−4926.

(28) Hu, D.; Cheng, G.; Liu, H.; Lv, Y.; Lu, P.; Ma, Y. Carbazole/Oligocarbazoles Substituted Silanes as Wide Bandgap Host Materials for Solution-Processable Electrophosphorescent Devices. *Org. Electron.* **2012**, *13*, 2825−2831.

(29) Yin, C.; Ye, S.; Zhao, J.; Yi, M.; Xie, L.; Lin, Z.; Chang, Y.; Liu, F.; Xu, H.; Shi, N.; Qian, Y.; Huang, W. Hindrance-Functionalized $\pi$-Stacked Polymer Host Materials of the Cardo-Type Carbazole-Fluorene Hybrid for Solution-Processable Blue Electrophosphorescent Devices. *Macromolecules* **2011**, *44*, 4589−4595.

(30) Li, H.; Wang, Y.; Yuan, K.; Tao, Y.; Chen, R.; Zheng, C.; Zhou, X.; Li, J.; Huang, W. Efficient Synthesis of $\pi$-Extended Phenazasilines for Optical and Electronic Applications. *Chem. Commun.* **2014**, *50*, 15760−15763.

(31) Han, C.; Zhao, F.; Zhang, Z.; Zhu, L.; Xu, H.; Li, J.; Ma, D.; Yan, P. Constructing Low-Triplet-Energy Hosts for Highly Efficient Blue Pholeds: Controlling Charge and Exciton Capture in Doping Systems. *Chem. Mater.* **2013**, *25*, 4966−4976.

(32) Brunner, K.; Van Dijken, A.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Tuning the Homo Level without Influencing the Triplet Energy in Small Molecules. *J. Am. Chem. Soc.* **2004**, *126*, 6035−6042.

(33) Chen, R.; Xie, G.; Zhao, Y.; Zhang, S.; Yin, J.; Liu, S.; Huang, W. Novel Heterofluorene-Based Hosts for Highly Efficient Blue Electrophosphorescence at Low Operating Voltages. *Org. Electron.* **2011**, *12*, 1619−1624.

(34) Kim, D.; Coropceanu, V.; Brédas, J. Design of Efficient Ambipolar Host Materials for Organic Blue Electrophosphorescence: Theoretical Characterization of Hosts Based on Carbazole Derivatives. *J. Am. Chem. Soc.* **2011**, *133*, 17895−17900.

(35) Yin, J.; Zhang, S.; Chen, R.; Ling, Q.; Huang, W. Carbazole Endcapped Heterofluorenes as Host Materials: Theoretical Study of their Structural, Electronic, and Optical Properties. *Phys. Chem. Chem. Phys.* **2010**, *12*, 15448−15458.

(36) Sun, Y.; Giebink, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R. Management of Singlet and Triplet Excitons for Efficient White Organic Light-Emitting Devices. *Nature* **2006**, *440*, 908−912.

(37) Fan, M. G.; Yao, J. N. *Photochemistry and Optical Function Materials*; Science Press: China, 2009.

(38) Tandon, K.; Ramasesha, S.; Mazumdar, S. Electron Correlation Effects in Electron-Hole Recombination in Organic Light-Emitting Diodes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 45109.

(39) LESAGE, M.; SIMOES, J.; GRILLER, D. Triphenylsilane-A Useful Radical-Based Reducing Agent. *J. Org. Chem.* **1990**, *55*, 5413−5414.

(40) Huang, S.; Zhang, Q.; Shiota, Y.; Nakagawa, T.; Kuwabara, K.; Yoshizawa, K.; Adachi, C. Computational Prediction for Singlet-and Triplet-Transition Energies of Charge-Transfer Compounds. *J. Chem. Theory Comput.* **2013**, *9*, 3872−3877.

(41) Tang, C.; Bi, R.; Tao, Y.; Wang, F.; Cao, X.; Wang, S.; Jiang, T.; Zhong, C.; Zhang, H.; Huang, W. A Versatile Efficient One-Step Approach for Carbazole-Pyridine Hybrid Molecules: Highly Efficient Host Materials for Blue Phosphorescent Oleds. *Chem. Commun.* **2015**, *51*, 1650−1653.

(42) Sasabe, H.; Kido, J. Development of High Performance Oleds for General Lighting. *J. Mater. Chem. C* **2013**, *1*, 1699−1707.

(43) Wohlgenannt, M.; Tandon, K.; Mazumdar, S.; Ramasesha, S.; Vardeny, Z. V. Formation Cross-Sections of Singlet and Triplet Excitons in Pi-Conjugated Polymers. *Nature* **2001**, *409*, 494−497.