

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

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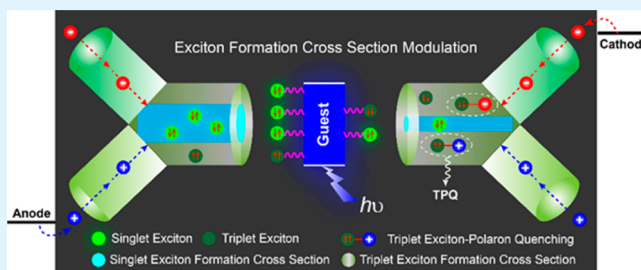
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Supporting Information

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 (\sim 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

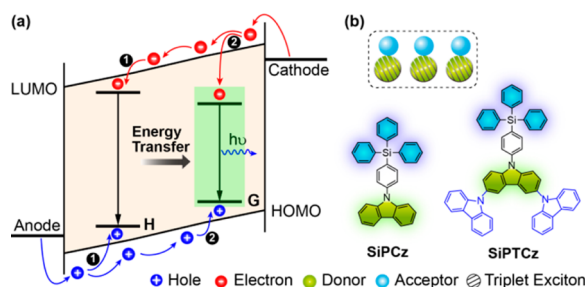
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groups, leading to overlapped energy transfer and charge transfer channels and thus the inevitable quenching effects of the host triplet excitons.

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



^aInset: 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 (\sim 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).

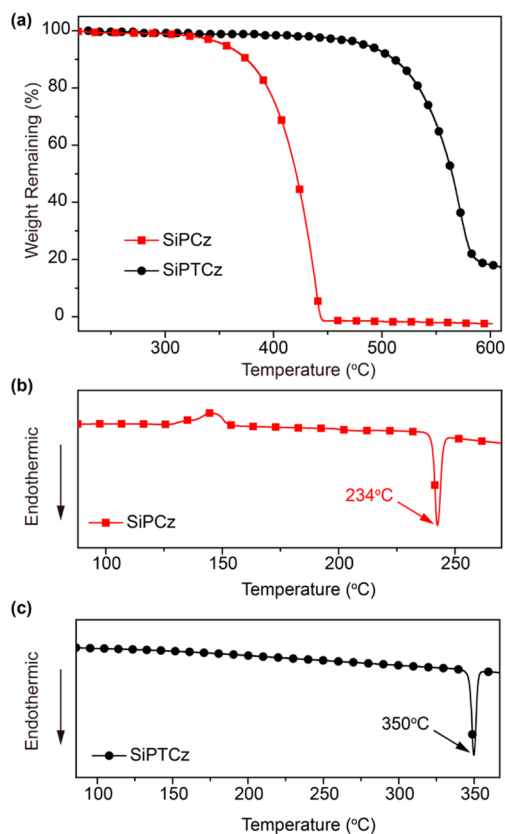


Figure 1. (a) TGA and (b and c) DSC curves (second heating) of SiPCz and SiPTCz.

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

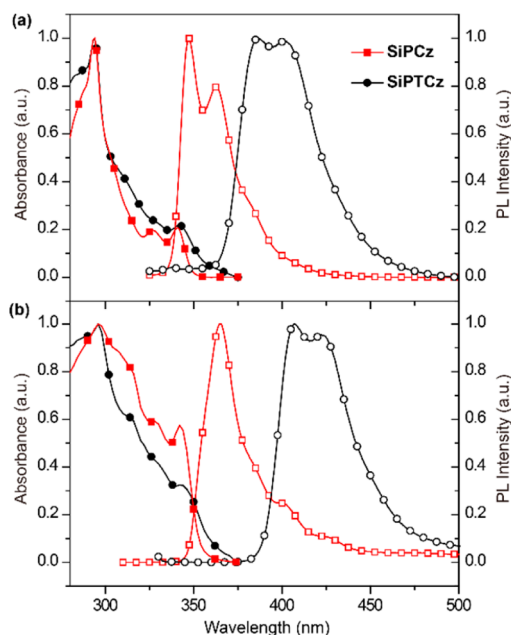


Figure 2. Absorption (closed symbols) and photoluminescence (open symbols, excited at 300 nm) spectra of SiPCz and SiPTCz (a) in dilute (1×10^{-5} mol L⁻¹) CH₂Cl₂ and (b) in thin film.

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 π -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)

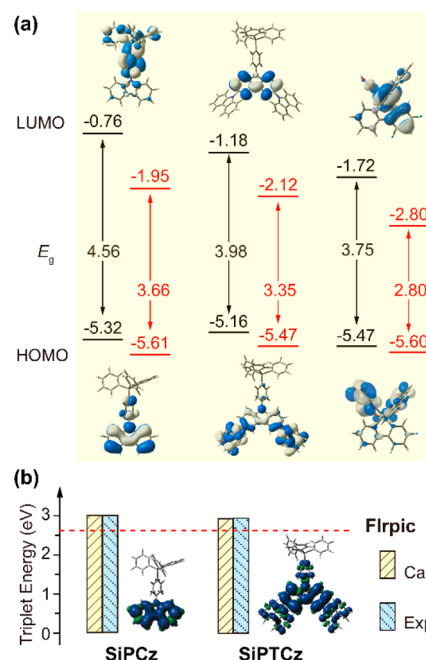


Figure 3. (a) DFT calculated (in black) and experimental (in red) HOMO and LUMO energy levels, bandgap (E_g) (in eV), (b) the lowest triplet (T_1) energies, and contours of the spin density distributions of the T_1 states of SiPCz and SiPTCz.

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 carbazolyis, 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)
		λ_{abs} (nm)	λ_{em} (nm)	PLQY	τ (ns)	λ_{abs} (nm)		λ_{em} (nm)	PLQY	τ (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		

^aAt 5% weight loss. ^bEstimated from the edge of the absorption spectrum in film.

carbazole in SiPTCz. In comparison with the HOMO and LUMO of Flrpic, 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 CH₂Cl₂ at 77 K after 5 ms delay (Figure 4). Such an E_T level is close to that of

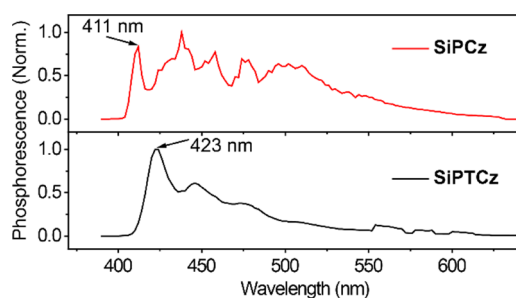


Figure 4. Phosphorescence spectra (excited at 337 nm) of SiPCz and SiPTCz at 77 K in CH₂Cl₂.

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 Flrpic (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) analysis³⁴ 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 (θ) 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 (χ_S) and triplet (χ_T) exciton formation fractions were studied.³⁵ Experimentally, a

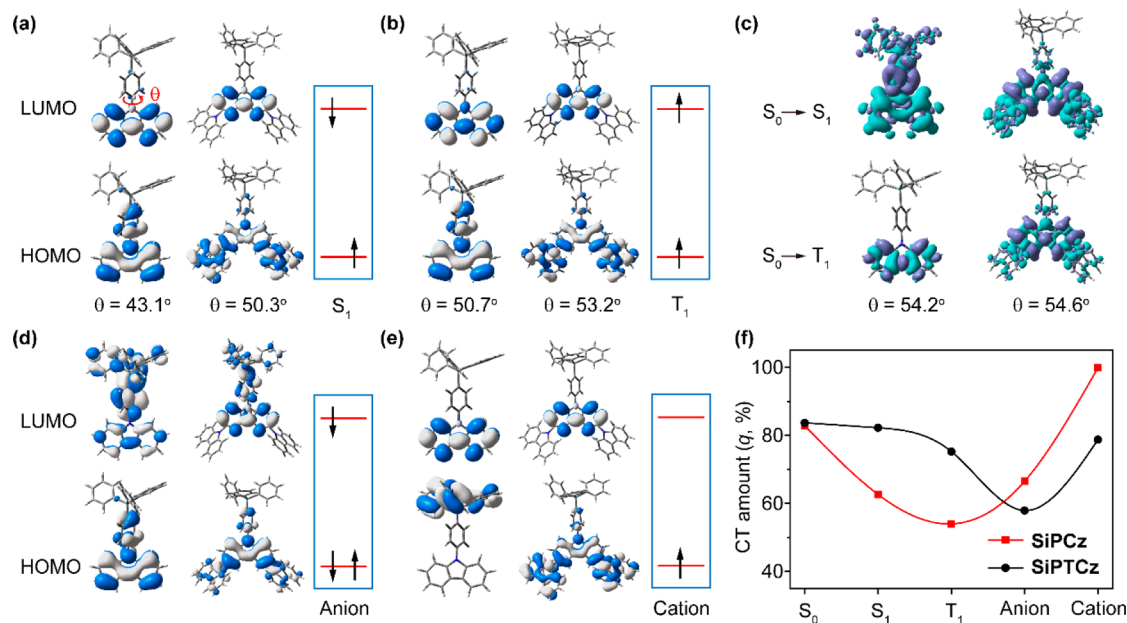


Figure 5. DFT calculated HOMO and LUMO distributions at optimized (a) S_1 , (b) T_1 , (d) anion, and (e) cation states; (c) change of electron-density distribution upon $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions based on S_0 state; and (f) CT amount of molecular structures at S_0 , S_1 , T_1 , cationic, and anionic states of SiPCz and SiPTCz. Inset shows θ 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 (χ_s) and Triplet (χ_T) Exciton Generation Fractions of SiPCz and SiPTCz

compd	CV (eV)		E_g	$^{exp}E_{T1}$ (eV)	$^{exp}E_{S1}$ (eV)	binding energy (eV)		χ_s (%)	χ_T (%)
	HOMO	LUMO				$^{exp}E_{bS}$	$^{exp}E_{bT}$		
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 χ_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 χ_s of SiPCz; therefore, better PhOLED device performance of SiPCz can be expected thermodynamically from suppressed generation of triplet exciton with low χ_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



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 (λ_+^S) and triplet (λ_+^T) excitons generated via the first way from $M^+ \rightarrow M^{S/T}$ and $M^- \rightarrow M_0$ and singlet (λ_-^S) and triplet (λ_-^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.

$$\lambda_+^{S/T} = \lambda_2 + \lambda_3 \quad (2)$$

$$\lambda_-^{S/T} = \lambda_1 + \lambda_4 \quad (3)$$

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

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

The significantly lower λ_s of SiPCz in both channels and especially the much lower λ_-^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.

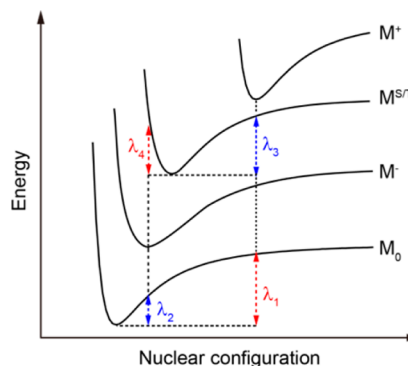


Figure 6. Calculation of reorganization energies of singlet and triplet excitons electronically excited in devices.

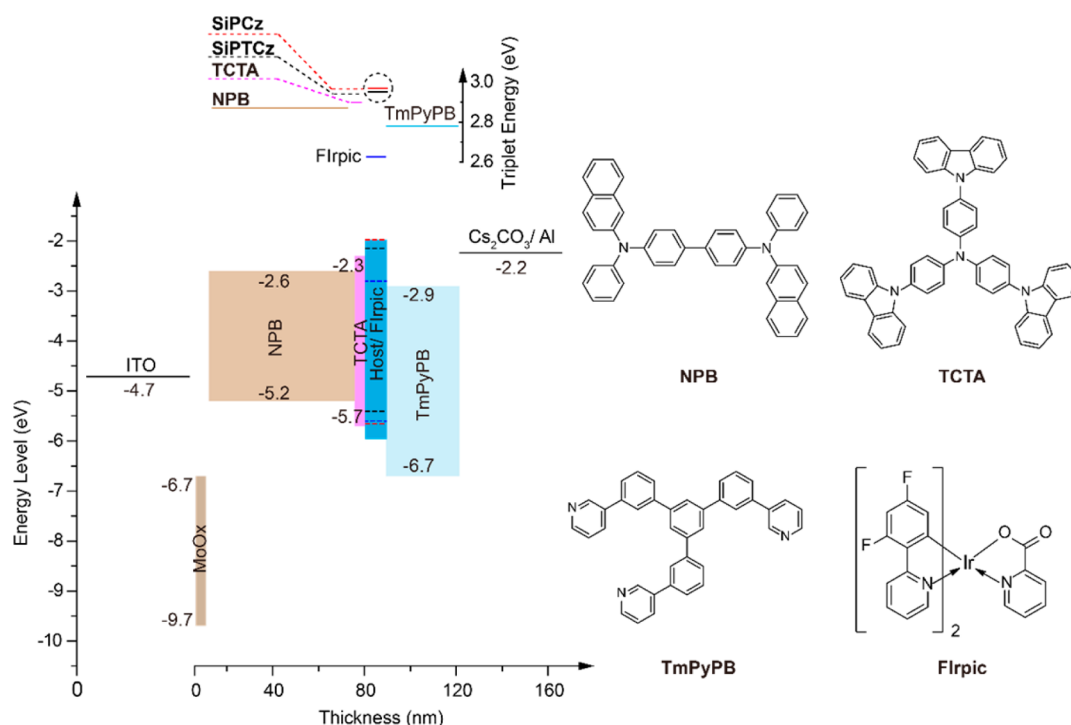


Figure 7. Blue PhOLED device configuration and energy level diagram using SiPCz and SiPTCz as the host materials and Flrpic as the guest material.

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 Flrpic were fabricated in a conventional configuration of ITO/MoO_x (5 nm)/NPB (70 nm)/TCTA (5 nm)/host:Flrpic (10 nm, 15%)/TmPyPB (35 nm)/Cs₂CO₃ (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 mobilities 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 Flrpic (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

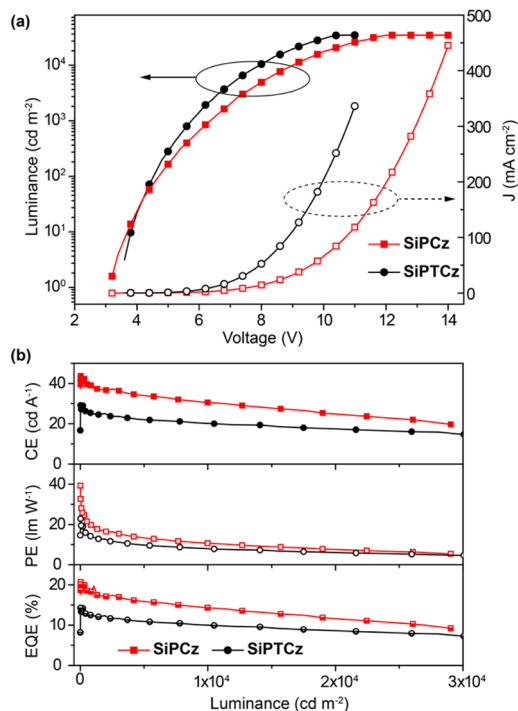


Figure 8. (a) Current density (*J*) (open)–luminance (solid)–voltage curves and (b) efficiency–luminance curves of the PhOLED devices.

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	operating voltage ^a (V)	max efficiency ^b	efficiency ^c			q^d (%)	χ_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

^aIn the order of 1, 100, and 1000 cd m⁻². ^bIn the order of CE (cd A⁻¹), PE (lm W⁻¹), and EQE (%). ^cIn the order of 100 and 1000 cd m⁻². ^dCT amount (q) at anionic and cationic states. ^eTriplet exciton formation fraction (χ_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 χ_S and λ_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 (η_S) of SiPCz and SiPTCz based fluorescent OLEDs were found to be 17.6% and 7.9%, respectively (eq S20). The significantly higher η_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 χ_S and low λ_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 the rational development of advanced optoelectronic organic semiconductors.

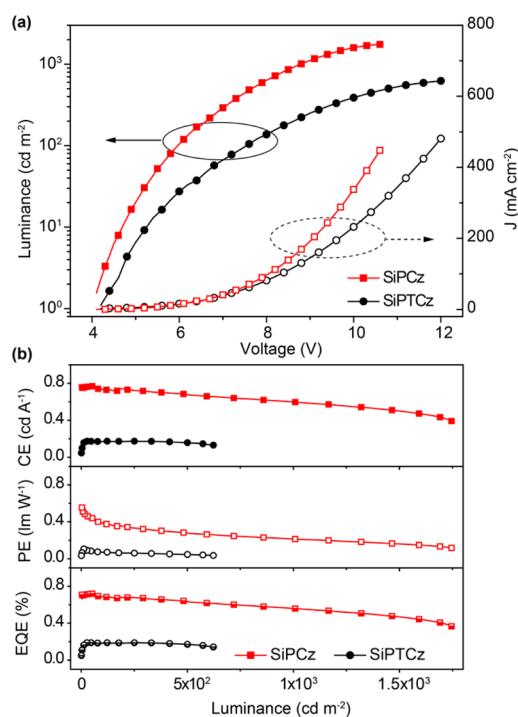


Figure 9. (a) Current density (J) (open)–luminance (solid)–voltage curves and (b) efficiencies–luminance curves of the FIrpic-free devices.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10806.

Detailed synthesis, characterization data, experimental methods, and photophysical property measurements (DSC, TGA, cyclic voltammetry, and atom force microscopy) of the organic molecules, and calculations of exciton generation fractions, electron-density changes, device fabrication, and measurements (PDF)

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Notes

The authors declare no competing financial interest.

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