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Non-doped organic light-emitting diodes based on phenanthroimidazole-triphenylamine derivatives with a low efficiency roll-off of 9% at a high luminance of 10000 cd m⁻²

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Simultaneously achieving high exciton utilization efficiency (η_s) and low efficiency roll-off at high brightness is challenging for fluorescent organic light-emitting diodes (OLEDs). In this work, we tried to realize this goal by constructing "hot exciton" materials via fine-tuning the lowest triplet excited state (T_1) characters. Two phenanthroimidazole-triphenylamine based donor-acceptor (D-A) derivatives TPPI-AQ and TPPI-BZPCN have been designed and synthesized. The photophysical studies and theoretical calculations reveal that TPPI-BZPCN has an obvious "hot exciton" feature and aggregation-induced emission (AIE) characteristic. A big gap between T_1 and T_2 exists in TPPI-BZPCN which provides the possibility for reverse intersystem system crossing (RISC) process from upper energy level of T_2 to S_1 . As a result, the non-doped electroluminescent device based on TPPI-BZPCN achieves a maximum external quantum efficiency (EQE) of 3.33%. The electroluminescence (EL) spectrum exhibits an emission peak at 592 nm, and the brightness can be up to 55657 cd m⁻². Also, the device is able to remain EQE of 3.03% at the high luminance of 10000 cd m⁻², with a very low efficiency roll-off of 9%, which is the lowest efficiency roll-off currently reported in the orange-red emitters based on "hot exciton" mechanism. Moreover, the η_s of the non-doped device reaches 48%, which exceeds the limitation of 25% in conventional fluorescence OLEDs.

Introduction

Organic light-emitting diodes (OLEDs) have attracted great attentions and considered as the next generation flat-panel displays and white lighting technologies owing to their unique features such as flexibility, lightweight, superior color gamut, no turn-on delay and wide viewing angle.¹⁻⁶ Tremendous efforts have been made to accelerate the development and commercialization of OLEDs. How to maximize the exciton utilization efficiency (η_s) is the crucial issue to improve the performance of OLEDs.^{7,8} For this purpose, phosphoresceence,⁹⁻¹³ thermally activated delayed fluorescence (TADF),^{1,14-16} triplet-triplet annihilation (TTA),¹⁷⁻¹⁹ "hot exciton"²⁰ and radicals²¹⁻²³ represent the main approaches to make use of triplet excitons. Among them, TADF and "hot exciton" materials, which are metal-free, relatively easy to synthesize and able to obtain 100% internal quantum efficiency theoretically, have been rapidly developed in recent years. Materials with relatively wide bandgaps such as blue and green emitters based on these two mechanisms are well-developed and some materials have been reported to show excellent performance in OLED applications.²⁴⁻²⁸ However, materials with narrower bandgaps, including orange and red emitters with good OLED performance still remain challenging.

According to the energy gap law, a narrow bandgap between the lowest singlet excited state (S₁) and the ground state (S₀) will result in a severe nonradiative internal conversion (IC), which inevitably leads to lower photoluminescent quantum yield (PLQY).²⁹⁻³¹ Besides, the character of lowest triplet excited state (T_1) has a crucial influence on the property of the resulting materials. A donor-acceptor design strategy is commonly used to achieve emitter with narrow bandgap. In general, the T_1 value of the whole molecule is determined by the lowest T_1 of respective building blocks. In fact, in the design of TADF materials, the constructing unit with low T₁ energy of localized state (³LE) should be avoided because the ³LE tends to weaken or even quench the delayed fluorescence due to the spin forbidden transition and big energy difference when ³LE is converted to S₁ of charge transfer state (¹CT).³² In this case, some traditional electron-withdrawing units with low T₁ values are not suitable for construction of TADF materials but may show potential applications in the design of "hot exciton" materials since the reverse intersystem system crossing (RISC) process occurs in the upper level and T₁ value shows almost no effect on the harvesting of triplet excitons. Also, as compared with TADF materials which suffer from the low PLQYs due to the separated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels and rapid efficiency roll-offs at high brightness (>1000 cd m⁻²)^{14,33-36} on account of the accumulation of triplet excitons, materials based on "hot exciton" possess relatively high PLQYs, short fluorescent lifetimes, and usually show ideal efficiency roll-offs in OLEDs.^{20,37-40} The "hot exciton" material with narrower bandgap needs further investigation.41-43

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In this work, we tried to obtain "hot exciton" materials by fine-tuning the T_1 characters of electron acceptors. Benzothiadiazole (BZP) is a five-membered heterocyclic ring that contains two sp² non-equivalent hybridized nitrogen atoms and one sp equivalent hybridized sulfur atom. BZP is a classical electron-withdrawing group with a $T_{\rm 1}$ lower than 2.0 eV. Moreover, BZP possesses a high PLQY and a large energy gap between T_1 and T_2 (0.9 eV), which will facilitate the realization of the "hot exciton" feature. Here, the cyano group, which possesses a higher T₁ than BZP, is adopted to connect with BZP to form a stronger electron acceptor, cyano-substituted BZP (BZPCN), aiming at extending the emission wavelength of the resulting molecule. In our prior studies, phenanthroimidazole (PI) is found to have decent PLQY and excellent thermal stability owing to the rigid planar π conjugation.¹⁹ The intrinsically bipolar electronic structure of PI is beneficial to achieve balanced charge transport and high performance in OLEDs.44,45 According to previous works, connecting acceptor at the C2 position and donor at the N1 position of PI core will be benefit for achieving high-performance PI-based bipolar emitters.46 Herein, we further introduce triphenylamine (TPA) at the N1 position of PI unit. Thus, TPA and PI are combined to form a whole stronger new donor (TPPI). The propeller-shaped structure of TPA can sterically inhibit the π - π molecular stacking and avoid aggregation induced quenching (ACQ) in the solid state⁴⁷ as well as partially increase the solubility of molecules for lowering the difficulty of purification. TPPI-BZPCN is thus designed with the expectation to be a "hot exciton" material with low T_1 value. Besides, another acceptor anthraquinone (AQ), which has better electron-withdrawing ability deriving from the existence of two carbonyl groups but possesses a higher T₁ of 2.5 eV, is also selected as constructing unit to replace BZPCN group to get TPPI-AQ for comparison purpose. As a result, experimental investigations demonstrate that TPPI-BZPCN owns obvious "hot exciton" state feature and aggregation-induced emission (AIE) characteristic. Theoretical calculations indicate a low T₁ in TPPI-BZPCN which facilitate to enlarge the energy gap between the T_1 and T_2 . The "hot exciton" character is not observed in TPPI-AQ due to the higher T₁ energy and resulting much more IC processes among T_1 and T_n .

The non-doped device based on TPPI-BZPCN shows a high η_{S} of 48% and a high brightness of 55657 cd m⁻². Moreover, the non-doped device achieves a maximum external quantum efficiency (EQE) of 3.33% at 1000 cd m⁻², and remains EQE of 3.03% at the high luminance of 10000 cd m⁻², with a very low efficiency roll-off of 9%. These results suggesting the non-doped device keeps relatively high efficiency as well as a low efficiency roll-off at high brightness.

Results and Discussion

Synthesis and Characterization

The molecular structures and synthesis routes of TPPI-BZPCN and TPPI-AQ are shown in **Scheme 1**. TPPIBr was first prepared by the one-pot reaction,⁴⁸ in which TPA-NH₂, 4-bromobenzaldehyde and phenanthrene-9,10-dione were



Scheme. 1 Synthesis routes for TPPI-BZPCN and TPPI-AQ.

(a) Suzuki coupling: Pd (PPh₃)₄, K₂CO₃ (2 M aq), toluene, 90 °C, 36 h under N₂ atmosphere; (b) CsF, DMSO, 140 °C, N₂ protection, 6 h; (c) SnCl₂ • 2H₂O, CH₃CH₂OH, N₂ protection, 70 °C, 100 min; (d) CH₃COONH₄, acetic acid, 120 °C, N₂ protection, 2 h; (e) bis(pinacolato)diboron, Pd (dppf) Cl₂, KOAc, 1,4-dioxane, 90 °C, N₂ protection, 48 h.

refluxed in acetic acid. Then, TPPIB was accessible through reaction between bis(pinacolato)diboron and TPPIBr. Finally, TPPI-BZPCN was successfully synthesized by using BZPCNBr and TPPIB as reactants via palladium-catalyzed Suzuki coupling. Similarly, TPPI-AQ was obtained in the same way by employing TPPIB and 2-bromoanthracene-9,10-dione as starting materials. The molecular structures of TPPI-BZPCN and TPPI-AQ were characterized by mass spectrometry spectroscopy (MS), nuclear magnetic resonance (NMR) and elemental analysis, which are corresponded well with their predicted results.

Thermal properties

The thermal properties of TPPI-BZPCN and TPPI-AQ were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). For TPPI-BZPCN and TPPI-AQ, the thermal degradation temperatures (T_d) are



Fig. 1 (a) TGA and (b) DSC curves of TPPI-BZPCN and TPPI-AQ.

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estimated to be 508 and 473 °C (**Fig 1a**). Such high values of T_d indicate that TPPI-BZPCN and TPPI-AQ are suitable for fabricating OLEDs through evaporation methods and tolerant for joule heat generated during the preparation process. Additionally, only two slight endothermic signals were observed for TPPI-BZPCN and TPPI-AQ during the second heating scan (**Fig 1b**), which should be ascribed to glass transition temperatures (T_g) at 146 and 147 °C of TPPI-BZPCN and TPPI-AQ, respectively. However, no apparent crystallization temperatures (T_c) or melting points (T_m) were found during the increasing process of two components, indicating that TPPI-BZPCN and TPPI-AQ both show excellent morphological stability, which is in favour of OLED applications.

Theoretical Calculations

The S_0 and S_1 geometries for TPPI-BZPCN and TPPI-AQ were optimized by density functional theory (DFT) and timedependent density functional theory (TDDFT) methods at the basis set level of B3LYP/6-31G (d, p) to comprehend the relation between the molecular structure and the emission behavior of two materials. Their optimized geometry and structure parameters are shown in Fig. 2a. For ground state, the twist angles θ_1 between TPPI and phenyl bridge are 29° and 25° for TPPI-BZPCN and TPPI-AQ, and torsion angles θ_2 between bridging phenyl ring and two acceptors are both 35° for TPPI-BZPCN and TPPI-AQ. The two adjacent hydrogen atoms on the benzene bridge and the acceptor (BZPCN unit or AQ unit) have more robust space steric hindrance, resulting in a larger torsion angle θ_2 comparing to θ_1 . For the excited state of the two molecules, twist angles θ_1 and θ_2 change very little. As a result, the appropriate twist angles contribute to the increase of conjugated length and the generation of long wavelength emission. Also, the HOMO and LUMO orbits are mostly located on the donor and acceptor groups, respectively, and partially overlapped on the phenyl bridge (Fig. 2b), which will be beneficial to enhance the locally excited (LE) proportion and further improve the PLQY.

Then, we calculated natural transition orbital (NTO) to analyze electron transition characters for the emission of TPPI-BZPCN and TPPI-AQ. As shown in **Fig. 3a**, the particle for the S_1 state of TPPI-BZPCN is mainly dispersed on the acceptor BZPCN, but the hole is distributed over the long axis of TPPI-BZPCN which contains BZPCN and PI group, demonstrating the



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coexistence of LE and charge-transfer (CT) components. Meanwhile, the T_1 state of TPPI-BZPCN is ³LE state with a low energy value of 1.74 eV, which fits our original vision well.

Thanks to the low T₁ energy level, there is a significant energy gap (0.98 eV) between T_2 (2.72 eV) and T_1 (1.74 eV), as well as a negligible energy gap (0.03 eV) between T₂ (2.72 eV) and S₁ (2.69 eV). Thus, it provides the possibility to open up the RISC process from T_2 to S_1 and the IC from T_2 to T_1 may be effectively inhibited. These characters might endow TPPI-BZPCN with high PLQY and high η_s . As compared, the situation in TPPI-AQ is quite different from TPPI-BZPCN. As shown in Fig. 3b, the S₂ and T₄ states of TPPI-AQ manifest the coexistence of LE and CT components. However, the energy gap of T_4 (2.86 eV, Table S2) and T₃ (2.75eV) is 0.11 eV, and a relatively small energy gap (0.06 eV) is observed between T_1 (2.56 eV) and T_2 (2.62 eV), which is conducive to the sequential IC process from T_4 to T_1 . Eventually, the RISC process in the upper level states is greatly reduced, and plenty of triplet excitons would be lost through the non-radiative transition from T₁ to S₀. On the whole, compared with TPPI-AQ, TPPI-BZPCN can be expected to achieve both high PLQY and high n_s simultaneously, and further to maximize EQE in OLEDs. Therefore, a low-lying energy of T_1 as well as a large energy gap between T₁ and T₂ are essential for constructing "hot exciton" materials with high exciton utilization.

Photophysical Properties

Also, the ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra of TPPI-BZPCN and TPPI-AQ were measured in various solvents for further observation the ground state and the excited state properties. As shown in **Fig. S8**, the absorption



Fig. 3 (a) The natural transition orbitals for S₁, T₁, and T₂ and model for exciton relaxation process of TPPI-BZPCN. (b) The natural transition orbitals for S₁, S₂, T₃ and T₄, and model for exciton relaxation process of TPPI-AQ.

ARTICLE

spectra of TPPI-BZPCN and TPPI-AQ are kept almost unchanged with the increase of solvent polarity, indicating hardly variations for dipole distance of the ground state in different solvents. TPPI-BZPCN and TPPI-AQ have the same absorption peak at 363 nm, which arises from the $\pi\text{-}\pi^*$ transition of the PI moiety. For TPPI-BZPCN, the absorption band around 420 nm can be attributed to the intramolecular CT and the 307 nm absorption peak comes from the π - π * transition of BZP moiety. As for TPPI-AQ, the 311 nm absorption band is ascribed to the $\pi\text{-}\pi^*$ transition of AQ, and the 410 nm absorption peak can be attributed to the intramolecular CT. Besides, the absorption onsets of TPPI-BZPCN and TPPI-AQ in THF correspond to 497 and 487 nm, and the optical gaps are estimated to be 2.49 and 2.10 eV, respectively. The emission spectra of TPPI-BZPCN and TPPI-AQ are presented in Fig. 4. With the increase of solvent polarity, the emission spectra of the two molecules are gradually broadened as well as become structureless and redshifted, testifying the natural CT ingredient in their excited states.

In order to get a better insight into the property of excited state, the Lippert-Mataga relation was applied to plot the linear fitting analysis of the Stokes shifts (va-vf) and the orientation polarizability (f). The slope of the line is corresponding to the dipole moment (μ_e) of excited state.⁴⁹ As shown in Fig. S11, either TPPI-BZPCN and TPPI-AQ present a constant slope suggesting that the feature of S₁ hardly change; thus, both of them possess a quasi-equivalent hybridized excited state with evaluated dipole moments to be 18.9 D (r = 0.97) and 20.6 D (r = 0.94), respectively. These dipole moment values between the 23 D (typical CT compound DMABN) and 8 D (typical LE compound) are in consistent with the "hot exciton" character.⁵⁰ Moreover, in the measurement of transient PL decay, they both exhibit single-exponential lifetimes in nonpolar hexane solvent, which are 3.80 ns for TPPI-BZPCN and 1.75 ns for TPPI-AQ, respectively (Fig. S12). No long lifetime was observed in their films under degassed condition (Fig. S13). These results suggest these compounds are not emitters with delayed fluorescence.

The investigations of the AIE activity of TPPI-BZPCN and TPPI-AQ were also implemented. As shown in **Fig.5a** and **5b**, in 100% THF solution, TPPI-BZPCN exhibits an orange emission peaking at 563 nm. Once the f_w exceeds 0%, the emission intensity decreases rapidly. The emission intensity remains weakened until f_w increased to 60%, accompanied by slightly red-shifted emission peak. This can be interpreted by the effect

Table 1 Key thermal and photophysical properties of TPPI-BZPCN and TPPI-AQ.

Compound	T_{d}^{a}	T_{g}^{b}	HOMO/LUMO ^c	PLQY ^d	Eg e
	(°C)	(°C)	(eV)	(%)	(eV)
TPPI-BZPCN	508	146	-5.63/-3.37	35.0	2.49
TPPI-AQ	473	147	-5.64/-3.68	0.82	2.10

^a T_d is thermal-decomposition temperature at a weight percentage of 95%. ^b T_g is glass transition temperatures. ^c HOMO and LUMO levels were calculated using the oxidation onset potentials and the reduction onset potentials, respectively. ^d The absolute PL quantum yield of neat film estimated by integrating sphere. ^e Optical gap calculated from the absorption onset in dilute THF (10⁻⁵ M).



Fig. 4 Emission spectra of TPPI-BZPCN (a) and TPPI-AQ (b) in different solvents.

of intermolecular CT. When f_w is over 60%, the emission intensity is increased sharply with a gradual blue-shift in emission peaks owing to the AIE effect. These results attest that TPPI-BZPCN possesses AIE feature.^{8,40,51} As shown in **Fig. 5c** and **5d**, the PL intensity of TPPI- AQ remains low when the f_w is less than 80% in the THF/water mixture, but it increased rapidly when the f_w is up to 90%. The sudden increase of emission intensity of TPPI-AQ deriving from the strong aggregation limits the non-radiative transition caused by vibration and rotation, which is a commonly accepted mechanism of AIE phenomenon.⁵²⁻⁵⁵

The PLQY of TPPI-BZPCN in the nonpolar solvent n-hexane is 50%. However, no matter in nonpolar solvent or high polar solvent, the PLQY of TPPI-AQ is quite low, generally about only 0.5% (**Table S1**). This may arise from the enhanced nonradiative transition rate. The TPPI-BZPCN neat film shows an emission peak at 573 nm (**Fig. S10**), and the corresponding PLQY is 35%. However, the



Fig. 5 PL spectra of TPPI-BZPCN (a) and TPPI-AQ (c) (10×10^{-5} M) in THF/water mixtures with different water fractions (f_w). Plot of I₁ (emission intensity)/I₀ (emission intensity in THF solution) of TPPI-BZPCN (b) and TPPI-AQ (d) versus water content of the solvent mixture.

Page 4 of 8

Journal Name

Journal Name

PLQY of TPPI-AQ neat film is only 0.8% with an emission peak located at 610 nm. Then we calculated the radiative rate (kr) and nonradiative rate (knr) of neat film through the following equations,

$$k_{\rm r} = \frac{\Phi}{\tau} \tag{1}$$

$$k_{\rm nr} = \frac{1 - \Phi}{\tau} \tag{2}$$

where Φ stands for the PLQY, and τ denotes the transient fluorescent lifetime. Taking TPPI-BZPCN as an example, in neat film, the value of Φ is 35% (Table 1) and the τ is 10.17 ns (Fig. **S13**). The k_r value of TPPI-BZPCN is calculated to be $3.4 \times 10^7 \text{ s}^{-1}$, and the k_{nr} is 6.4 × 10⁷ s⁻¹. In the same way, the k_r and k_{nr} for TPPI-AQ are 4.0×10^5 and 4.8×10^7 s⁻¹, respectively. The data comparison between the two compounds is shown in the Fig. **S14**. For TPPI-BZPCN, the k_r and k_{nr} are similar on the same order of magnitude. In contrast, the k_{nr} of TPPI-AQ is two orders of magnitude larger than k_r, demonstrating that the exciton of S₁ returns to S₀ mainly by the nonradiative process. As a result, the PLQY of TPPI-AQ is quite low no matter in solution or the neat film, and it also accounts for the different AIE properties. Detailed information is summarized in Table S1.

Electrochemical properties

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Cyclic voltammetry (CV) measurements were performed to estimate the HOMO and the LUMO levels of TPPI-BZPCN and TPPI-AQ (Fig. 6). Nearly equal HOMO levels were found for TPPI-BZPCN (-5.63 eV) and TPPI-AQ (-5.64 eV), which are originated from their same donor group of TPPI. Differently, TPPI-AQ exhibits a LUMO energy level of -3.68 eV, which is much lower than that of TPPI-BZPCN (-3.37 eV). The shallower LUMO level of TPPI-BZPCN is attributed to the weaker electron-withdrawing ability of BZPCN relative to AQ. Moreover, the higher LUMO energy level of TPPI-BZPCN compared with TPPI-AQ is closer to the LUMO energy level of the classical electron transporting material 3,3'-(5'-(3-(pyridin-3-yl)phenyl)-[1,1':3',1"laver terphenyl]3,3"-diyl)dipyridine (TmPyPb, -2.7 eV), which is beneficial for electron transportation to the emitting layer and improve the device efficiency.

Electroluminescence Properties

In order to study their electroluminescence (EL) performances, two non-doped devices were fabricated with the configuration of ITO/HATCN (6 nm)/TAPC (30 nm)/TCTA (10 nm)/EML (20 nm)/TmPyPb (40 nm)/LiF (1 nm)/Al (100 nm), in which indium tin oxide (ITO) was anode, 1,4,5,8,9,11-hex-aazatriphenylenehexacarbonitrile (HATCN) and di-(4-(N.Nditolylamino)phenyl)cyclohexane (TAPC) were employed as hole injection and transportation layer, respectively. Tris(4carbazoyl-9-ylphenyl)amine (TCTA) was the exciton blocking layer, LiF and TmPyPb corresponded to electron injection and transportation layer, Al was applied as the cathode. TPPI-BZPCN and TPPI-AQ were used as emitting layers (EML). The nondoped device based on TPPI-BZPCN displays an EL spectrum peaking at 592 nm with a maximum luminance of 55657 cd m⁻² (Fig. 7b). It exhibits an extremely low turn-on voltage (V_{on}) of



Fig. 6 Cyclic voltammograms of TPPI-BZPCN and TPPI-AQ.

2.8 V. The maximum EQE is obtained at high luminescence of 1000 cd m⁻² of 3.33%, with only 9% roll-off even at high luminance of 10000 cd m⁻² (EQE = 3.03%). The efficiency roll-off is negligible when comparing to most orange-red TADF emitters, which suffer from serious efficiency roll-offs at high luminance (>1000 cd m⁻²). Although the non-doped device of TPPI-AQ exhibits red-shifted emission peaking at 632 nm in contrast to TPPI- BZPCN. Nevertheless, the EQE of the nondoped device of TPPI-AQ is only 0.48%, and the maximum luminance is 1396 cd m⁻². In addition, the device based on TPPI-AQ showed a very high Von of 4.1 V. The PLQY of TPPI-AQ neat film is only 0.82%, while the PLQY of TPPI-BZPCN neat film is 35%, nearly 42 times higher than TPPI-AQ, suggesting the luminance of device based on TPPI-AQ needs higher voltage to reach 1 cd m⁻². Thus, the TPPI-AQ-based device showed very high Von. The non-doped device based on TPPI-BZPCN is much superior to TPPI-AQ in performance. This may be attributed to the utilization of more triplet excitons for TPPI-BZPCN.





Fig. 7 (a) The energy level diagram and the used materials in the devices. (b) Normalized EL spectra and external quantum efficiency versus luminance curves of non-doped devices based on TPPI-BZPCN and TPPI-AQ. (c) Current density-voltage-luminance (J-V-L) curves.

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Table 2 Key performance parameters of the EL performances of OLEDs based on TPPI-BZPCN and TPPI-AQ.							View Article Online DOI: 10.1039/D0TC03379K	
Device	$V_{\text{on}}^{\ a}$	L _{max} ^b	CE_{max} ^c	PE _{max} ^d	EQE (%) ^e	$\lambda_{\text{max}}{}^{f}$	CIE g	
	(∨)	(cd m⁻²)	(cd A ⁻¹)	(lm W⁻¹)	max/1000/10000 cd m ⁻²	(nm)	(x, y)	
TPPI-BZPCN	2.8	55657	7.6	4.28	3.33/3.33/3.03	592	(0.53,0.46)	
TPPI-AQ	4.1	1396	0.51	0.36	0.48/0.08/	632	(0.47,0.52)	

^a Turn-on voltage at 1 cd m⁻². ^b Maximum luminance. ^c Maximum current efficiency. ^d Maximum power efficiency. ^e Maximum external quantum efficiency/1000/10000 cd m⁻². ^f EL emission peak of EL spectrum at 100 cd m⁻². ^g CIE coordinate of at 100 cd m⁻².

The exciton utilization efficiency of the devices can be evaluated according to the EQE equation of OLED as below.

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$$EQE = (\gamma \times \eta_{S} \times \Phi_{PL}) \times \eta_{out}$$
(3)

where γ is the recombination efficiency of injected electron and hole, which usually regards as 100% if the device is reasonably designed. η_{out} is light out-coupling efficiency (\approx 0.20), and Φ_{PL} is the PLQY of the emitting layer. For TPPI-BZPCN, the PLQY is 35%, η_S value of TPPI-BZPCN can be calculated to be 48%, which is well in excess of the limitation of 25% for radiative excitons in conventional fluorescent OLEDs. While the η_S of TPPI-AQ calculated in the same way is only 3%. As mentioned above, this significant various depends on different utilization efficiency of excitons which is highly determined by the T_1 characters. The EL device performances of non-doped EL devices are listed in **Table 2** for TPPI-BZPCN and TPPI-AQ.

Conclusions

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In conclusion, two new orange-red fluorescent emitters TPPI-BZPCN and TPPI-AQ have been successfully developed by incorporating PI and TPA to form a new donor and BZPCN/ AQ separately as acceptor. Benefiting from contributions of "hot exciton" in the upper level and AIE characteristic, the η_s value of non-doped device based on TPPI-BZPCN reaches 48%. Besides, the maximum EQE is 3.33%, which is acquired at the luminance of 1000 cd m⁻². Even at a high luminescence of 10000 cd m⁻², the EQE can remain 3.03%, with only 9% reduction, which is quite a small value of efficiency roll-off. Additionally, the luminance can be up to a maximum of 55657 cd m⁻². As far as we know, this is one of the best non-doped devices among orange-red materials in the mechanism of "hot excitons". Our experimental results may provide a new way for further realizing high η_s and low efficiency roll-off at high luminescence in terms of orange-red emitters, which based on "hot excitons" mechanism.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, Nature, 2012, 492, 234-238.
- C. W. Tang and S. A. VanSlyke, Appl Phys Lett, 1987, 51, 913-915.
- 3. K. Yoshida, P. P. Manousiadis, R. Bian, Z. Chen, C. Murawski, M. C. Gather, H. Haas, G. A. Turnbull and I. D. W. Samuel, *Nat. Commun.*, 2020, 11, 1171.
- 4. T. B. Nguyen, H. Nakanotani, T. Hatakeyama and C. Adachi, *Adv. Mater.*, 2020, 32, 1906614.
- Z. Huang, Z. Bin, R. Su, F. Yang, J. Lan and J. You, Angew. Chem. Int. Ed. 10.1002/anie.201915397.
- S. V. Dayneko, M. Rahmati, M. Pahlevani and G. C. Welch, J. Mater. Chem. C, 2020, 8, 2314-2319.
- C. Wang, X. Li, Y. Pan, S. Zhang, L. Yao, Q. Bai, W. Li, P. Lu, B. Yang, S. Su and Y. Ma, ACS Appl. Mater. Interfaces, 2016, 8, 3041-3049.
- T. Liu, L. Zhu, S. Gong, C. Zhong, G. Xie, E. Mao, J. Fang, D. Ma and C. Yang, *Adv. Opt. Mater.*, 2017, 5. 1700145.
- 9. Z. Chen, H. Zhang, D. Wen, W. Wu, Q. Zeng, S. Chen and W.-Y. Wong, *Chem. Sci.*, 2020, 11, 2342-2349.
- L. J. Sicard, H. C. Li, Q. Wang, X. Y. Liu, O. Jeannin, J. Rault-Berthelot, L. S. Liao, Z. Q. Jiang and C. Poriel, *Angew. Chem. Int. Ed.*, 2019, 58, 3848-3853.
- 11. L. S. Cui, Y. M. Xie, Y. K. Wang, C. Zhong, Y. L. Deng, X. Y. Liu, Z. Q. Jiang and L. S. Liao, *Adv. Mater.*, 2015, 27, 4213-4217.
- S. Ohisa, T. Takahashi, M. Igarashi, H. Fukuda, T. Hikichi, R. Komatsu, E. Ueki, Y. J. Pu, T. Chiba and J. Kido, *Adv. Funct. Mater.*, 2019, 29, 1808022.
- Q. Peng, A. Obolda, M. Zhang and F. Li, Angew. Chem. Int. Ed., 2015, 54, 7091-7095.
- Q. Zhang, H. Kuwabara, W. J. Potscavage, Jr., S. Huang, Y. Hatae, T. Shibata and C. Adachi, *J. Am. Chem. Soc.*, 2014, 136, 18070-18081.
- Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka and C. Adachi, Nat. Photonics., 2014, 8, 326-332.
- 16. Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki and C. Adachi, *J. Am. Chem. Soc.*, 2012, 134, 14706-14709.
- 17. R. leuji, K. Goushi and C. Adachi, Nat. Commun., 2019, 10, 5283.
- V. Jankus, C. J. Chiang, F. Dias and A. P. Monkman, *Adv. Mater.*, 2013, 25, 1455-1459.
- X. Tang, Q. Bai, T. Shan, J. Li, Y. Gao, F. Liu, H. Liu, Q. Peng, B. Yang, F. Li and P. Lu, *Adv. Funct. Mater.*, 2018, 28, 1705813.
- Y. Xu, X. Liang, X. Zhou, P. Yuan, J. Zhou, C. Wang, B. Li, D. Hu, X. Qiao, X. Jiang, L. Liu, S. J. Su, D. Ma and Y. Ma, *Adv. Mater.*, 2019, 31, 1807388.
- 21. X. Ai, E. W. Evans, S. Dong, A. J. Gillett, H. Guo, Y. Chen, T. J. H. Hele, R. H. Friend and F. Li, *Nature*, 2018, 563, 536-540.
- 22. H. Guo, Q. Peng, X. K. Chen, Q. Gu, S. Dong, E. W. Evans, A. J. Gillett, X. Ai, M. Zhang, D. Credgington, V. Coropceanu, R. H.

Journal Name

Friend, J. L. Bredas and F. Li, Nat. Mater., 2019, 18, 977-984.

- 23. X. Ai, Y. Chen, Y. Feng and F. Li, *Angew. Chem. Int. Ed.*, 2018, 57, 2869-2873.
- T. A. Lin, T. Chatterjee, W. L. Tsai, W. K. Lee, M. J. Wu, M. Jiao, K. C. Pan, C. L. Yi, C. L. Chung, K. T. Wong and C. C. Wu, *Adv. Mater.*, 2016, 28, 6976-6983.
- 25. D. R. Lee, B. S. Kim, C. W. Lee, Y. Im, K. S. Yook, S. H. Hwang and J. Y. Lee, *ACS Appl. Mater. Interfaces*, 2015, 7, 9625-9629.
- 26. H. Liu, L. Kang, J. Li, F. Liu, X. He, S. Ren, X. Tang, C. Lv and P. Lu, *Nat. Photonics.*, 2019, 7, 10273-10280.
- T. Serevicius, R. Skaisgiris, J. Dodonova, L. Jagintavicius, D. Banevicius, K. Kazlauskas, S. Tumkevicius and S. Jursenas, ACS Appl. Mater. Interfaces, 2020, 12, 10727-10736.
- 28. T.-L. Wu, M.-J. Huang, C.-C. Lin, P.-Y. Huang, T.-Y. Chou, R.-W. Chen-Cheng, H.-W. Lin, R.-S. Liu and C.-H. Cheng, *Nat. Photonics.*, 2018, 12, 235-240.
- 29. Q. Zhao and J. Z. Sun, J. Mater. Chem. C, 2016, 4, 10588-10609.
- Z. Zhao, J. Geng, Z. Chang, S. Chen, C. Deng, T. Jiang, W. Qin, J. W. Y. Lam, H. S. Kwok, H. Qiu, B. Liu and B. Z. Tang, *J. Mater. Chem.*, 2012, 22, 11018-11021.
- J. H. Kim, J. H. Yun and J. Y. Lee, Adv. Opt. Mater., 2018, 6, 1800255.
- S. Zhang, L. Yao, Q. Peng, W. Li, Y. Pan, R. Xiao, Y. Gao, C. Gu,
 Z. Wang, P. Lu, F. Li, S. Su, B. Yang and Y. Ma, *Adv. Funct. Mater.*, 2015, 25, 1755-1762.
- 33. F. M. Xie, H. Z. Li, G. L. Dai, Y. Q. Li, T. Cheng, M. Xie, J. X. Tang and X. Zhao, ACS Appl. Mater. Interfaces, 2019, 11, 26144-26151.
- 34. G. Xie, X. Li, D. Chen, Z. Wang, X. Cai, D. Chen, Y. Li, K. Liu, Y. Cao and S. J. Su, Adv. Mater., 2016, 28, 181-187.
- J. X. Chen, W. W. Tao, W. C. Chen, Y. F. Xiao, K. Wang, C. Cao, J. Yu, S. Li, F. X. Geng, C. Adachi, C. S. Lee and X. H. Zhang, *Angew. Chem. Int. Ed.*, 2019, 58, 14660-14665.
- C. M. Hsieh, T. L. Wu, J. Jayakumar, Y. C. Wang, C. L. Ko, W. Y. Hung, T. C. Lin, H. H. Wu, K. H. Lin, C. H. Lin, S. Hsieh and C. H. Cheng, ACS Appl. Mater. Interfaces, 2020, 12, 23199-23206.
- 37. F. Liu, X. Man, H. Liu, J. Min, S. Zhao, W. Min, L. Gao, H. Jin and P. Lu, J. Mater. Chem. C, 2019, 7, 14881-14888.
- H. Liu, Q. Bai, L. Yao, H. Zhang, H. Xu, S. Zhang, W. Li, Y. Gao, J. Li, P. Lu, H. Wang, B. Yang and Y. Ma, *Chem Sci*, 2015, 6, 3797-3804.
- 39. X. Han, Q. Bai, L. Yao, H. Liu, Y. Gao, J. Li, L. Liu, Y. Liu, X. Li, P. Lu and B. Yang, *Adv. Funct. Mater.*, 2015, 25, 7521-7529.
- 40. T. Liu, L. Zhu, C. Zhong, G. Xie, S. Gong, J. Fang, D. Ma and C. Yang, *Adv. Funct. Mater.* 2017, 27, 1606384.
- 41. L. Yao, S. Zhang, R. Wang, W. Li, F. Shen, B. Yang and Y. Ma, Angew. Chem. Int. Ed., 2014, 53, 2119-2123.
- 42. F. Liu, Y. Tan, H. Liu, X. Tang, L. Gao, C. Du, J. Min, H. Jin and P. Lu, J. Mater. Chem. C, 2020, 8, 6883-6890.
- W. Li, Y. Pan, R. Xiao, Q. Peng, S. Zhang, D. Ma, F. Li, F. Shen, Y. Wang, B. Yang and Y. Ma, *Adv. Funct. Mater.*, 2014, 24, 1609-1614.
- W.-C. Chen, Z.-L. Zhu and C.-S. Lee, Adv. Opt. Mater., 2018, 6, 1800258.
- 45. W.-C. Chen, Q.-X. Tong, C.-S. Lee, *Sci. Adv. Mater.* 2015, 7, 2193.
- 46. J.-J. Zhu, Y. Chen, Y.-H. Xiao, X. Lian, G.-X. Yang, S.-S. Tang, D. Ma, Y. Wang and Q.-X. Tong, *J. Mater. Chem. C*, 2020, 8, 2975-2984.
- M. P. d. Cunha, T. T. Do, S. D. Yambem, H. D. Pham, S. Chang, S. Manzhos, R. Katoh and P. Sonar, *Mater Chem Phys*, 2018, 206, 56-63.
- 48. Z. Wang, P. Lu, S. Chen, Z. Gao, F. Shen, W. Zhang, Y. Xu, H. S. Kwok and Y. Ma, *J. Mater. Chem.*, 2011, 21, 5451-5456.
- 49. Z. R. Grabowski and K. Rotkiewicz, *Chem. Rev.*, 2003, 103, 3899-4031.
- S. Zhang, W. Li, L. Yao, Y. Pan, F. Shen, R. Xiao, B. Yang and Y. Ma, *Chem. Commun.*, 2013, 49, 11302-11304.

- W. Z. Yuan, Y. Gong, S. Chen, X. Y. Shen, J. W. Y. Lan, P. Lu, Y. Lu, Z. Wang, R. Hu, N. Xie, H. S. Kwok, <u>Apaness J. D. Surganos</u> B. Z. Tang, *Chem. Mater.*, 2012, 24, 1518-1528.
- 52. Y. Dong, J. W. Y. Lam, A. Qin, J. Liu, Z. Li, B. Z. Tang, J. Sun and H. S. Kwok, *Appl. Phys. Lett.* 2007, 91, 011111.
- R. Hu, E. Lager, A. Aguilar-Aguilar, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Zhong, K. S. Wong, E. Pena-Cabrera and B. Z. Tang, *J. Phys. Chem. C*, 2009, 113, 15845-15853.
- 54. X. Y. Shen, W. Z. Yuan, Y. Liu, Q. Zhao, P. Lu, Y. Ma, I. D. Williams, A. Qin, J. Z. Sun and B. Z. Tang, J. Phys. Chem. C, 2012, 116, 10541-10547.
- 55. J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin and Z. Li, *Adv. Funct. Mater*, 2013, 23, 2329-2337.

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The "hot exciton" material TPPI-BZPCN is successfully achieved by fine-tuning the T₁ characters of electron acceptor. The non-doped device based on TPPI-BZPCN exhibits a maximum EQE of 3.33% at the luminance of 1000 cd m⁻², and remains 3.03% at a high luminescence of 10000 cd m⁻², with an $00\pi4939\%$ reduction. Additionally, the luminance can reach a maximum of 55657 cd m⁻².

