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The development of high efficiency orange-red/red thermally activated delayed fluorescence (TADF) organic light emitting diodes (OLEDs) with reduced efficiency roll-off retains a huge challenge. By fusing two weak electron-withdrawing benzoyl and quinoxaline units into one molecule, a strong π -accepting phenyl(quinoxalin-6-yl)methanone unit is introduced as acceptor to develop three orange-red to red TADF emitters, (2-(4-(phenoxazin-10-yl)phenyl)quinoxalin-6-yl)phenylmethanone (**PXZ-PQM**), (2,3-bis(4-(phenoxazin-10-yl)phenyl)quinoxalin-6-yl)(phenyl)methanone (**DPXZ-PQM**) and (3,6-di(phenoxazin-10-yl)dibenzophenazin-11-yl)phenylmethanone (**DPXZ-DPPM**). By tuning the numbers of the donor and the electron withdrawing character of the acceptor, the emission wavelength can be regulated from orange-red to red (592-642 nm). The rigid planar constituent moieties and highly twisted molecular structures induce high photoluminescence quantum yields of 61-88% in doped films and extremely small singlet-triplet energy splitting. The orange-red TADF-OLED using **DPXZ-PQM** as an emitter achieves a maximum external quantum efficiency (EQE) as high as 26.0% at 590 nm, which is among the highest EQE values reported for orange-red TADF-OLEDs with similar wavelength. More importantly, a low efficiency roll-off is rendered with EQEs of 20.1 and 13.7% at a luminance of 100 and 1000 cd m⁻², respectively.

Introduction

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Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) materials without any noble-metal are raising ever-increasing interest due to their potential in achieving 100% internal quantum efficiency (IQE) in theory via efficient up-conversion from non-radiative triplet (T_1) to radiative singlet (S_1) .^{1, 2} Over the past few years, the record-high external quantum efficiencies (EQEs) of 38.15 ± 0.42 and $37.8\pm0.6\%$ have been realized for blue and green TADF-OLEDs, respectively.^{3, 4} In contrast, the EQEs of orange-red to red TADF-OLEDs with emission maxima beyond 580 nm rarely exceed 25%.⁵⁻⁷ The most decisive reason is that the overlap of vibration coupling between ground state and excited state will increase upon the decrease of energy gap and thereby decreases the photoluminescence quantum yields (PLQYs) of the emitters according to the energy-gap law.⁸ On the other hand, a small singlet-triplet energy splitting (ΔE_{ST}) is essential for efficient RISC process.^{9, 10} In general, small ΔE_{ST} can be realized by minimizing the overlap integral between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).^{11, 12} However, according

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to the Franck-Condon transition principle, small orbital overlap means a small probability of electronic transition and thereby decreases the oscillator strength (f) between the S₁ and ground (S_0) states, which is not conducive to obtain high PLQY.13 Therefore, this is a contradiction between realizing simultaneously the efficient reverse intersystem crossing (RISC) process and the high PLQY in the one molecule for efficient orange-red/red TADF emitters. Many efforts have been devoted towards exploiting highly efficient orangered/red TADF molecules, such as increasing the twist angle between the donor and acceptor by introducing multiple donors or acceptors, adjusting donor and acceptor strength of the molecule, and enlarging the molecular rigidity.¹⁴⁻¹⁷ A rigid planar 1,8-naphthalimide derivative based orange-red TADF-OLED has achieved a state-of-the-art EQE of 29.2% by Yang and co-worker, which is the most efficient orange-red/red TADF-OLED reported to date.⁵ Unfortunately, the device showed the serious efficiency roll-off at high current density due to the presence of triplet-triplet or singlet-triplet exciton annihilation. Therefore, the development of high efficiency orange-red to red TADF-OLEDs with reduced efficiency roll-off is a severe challenge for OLED application.

In this work, we designed and synthesized three orange-red to red TADF emitters, named (2-(4-(phenoxazin-10yl)phenyl)quinoxalin-6-yl)phenylmethanone (**PXZ-PQM**), (2,3bis(4-(phenoxazin-10-yl)phenyl)quinoxalin-6-yl) (phenyl)methanone (**DPXZ-PQM**) and (3,6-di(phenoxazin-10yl)dibenzophenazin-11-yl)phenylmethanone (**DPXZ-DPPM**). As we all know, benzoyl and quinoxaline units are often used as

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[†] Electronic Supplementary Information (ESI) available: TGA, DSC, CV curves, additional emission spectra, transient decay curves of the doped films, additional electroluminescence data of the OLED devices and crystal data. CCDC 1943981. See DOI: 10.1039/x0xx00000x

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Scheme 1 Synthetic procedures and chemical structures of PXZ-PQM, DPXZ-PQM and DPXZ-DPPM.

the acceptor moieties in high efficiency blue and green TADF emitters due to their weak electron withdrawing character.¹⁸⁻²⁰ Through integrating benzoyl and quinoxaline units into one molecule to strengthen the acceptor capacity, two acceptor cores. phenyl(quinoxalin-6-yl)methanone (POM) and dibenzo[a,c]phenazin-11-yl(phenyl)methanone (DPPM) with stronger electron withdrawing character are developed. PXZ is employed as the electron donor segments because of its strong electron-donating ability and rigid structure. These emitters show orange-red to red emissions with high PLQYs, small ΔE_{ST} values, and excellent TADF properties. The **DPXZ**-PQM-based electroluminescence (EL) device achieves an EQE as high as 26.0% with an orange EL peaking 590 nm, which represents the state-of-the-art device performance for orange-red TADF-OLEDs. More importantly, this device indicates a decent efficiency roll-off and their EQEs still maintained as 20.1 and 13.7% at a luminance of 100 and 1000 $\,$ cd m⁻², respectively. This study not only obtains a record-high EQE in orange-red TADF-OLEDs, but also provides a feasible pathway for constructing highly efficient orange-red/red TADF emitters

1. Results and discussion

Synthesis and Characterization

The molecular structures and synthetic procedures of the three emitters are shown in Scheme 1. The key intermediates Br-PQM, DBr-PQM and DBr-DPPM were synthesized via the cyclization reaction, followed by the Buchwald-Hartwig cross-coupling reaction to prepare the three TADF emitters (**PXZ-PQM, DPXZ-PQM** and **DPXZ-DPPM**) in good yields. Finally, these target compounds were further purified by vacuum

sublimation approach. The chemical structures of these compounds were fully characterized and confirmed by ¹H and ¹³C NMR, mass spectrometry, and elemental analysis. Their synthetic details and characteristics data are described in the Experimental Section.

Single Crystal Structures Analysis

To further make out structure-properties relationship, we grew single crystals of PXZ-PQM from the mixture solvent of methylene chloride and methanol. As shown in Fig. 1a, the dihedral angle between PQM group and phenylene linker is 31.1° and that between phenylene linker and PXZ moiety is 74.9°, indicating a highly twisted structure for the conjugated framework of PXZ-PQM. Two consecutive large twisted angles along the donor and acceptor groups are likely the key for the HOMO and LUMO separation. Each molecule shows two types of $\pi \cdots \pi$ interactions, one is between the PXZ donor in a small overlap area with a distance of 3.471 Å (Fig. 1c and 1d), and the other one between the PQM acceptors shows a weak interaction with a distance of 3.745 Å (Fig. 1b and 1d). In addition, the three-dimensional framework is formed based on the multiple hydrogen bonding interactions of C-H---O and C-H…N to stabilize the crystal and suppress non-radiative transition (Fig. 1e). Whole crystal data of PXZ-PQM are shown in Table S1.

Density Functional Theory (DFT) Calculations

To better understand electronic structures and the frontier molecular orbital distributions of these emitters, the quantumchemical calculations were carried out using the Gaussian 16 program package with the B3LYP/6-31G(d) level in the gas phase. The optimized geometries and the HOMO and LUMO distributions of these compounds are depicted in Fig. 2. For



Fig. 1 Single crystal structure (a), packing mode (b, c) and intermolecular interaction (d, e) of PXZ-PQM in single crystals.

PXZ-PQM, a small dihedral angle of 19.8° between the PQM acceptor and the adjacent phenylene linker is observed. As the increase of PXZ donors, the large steric hindrance induces DPXZ-PQM the larger dihedral angles of 52.7° and 53.2°. In addition, these three compounds exhibit similar highly twisted structures with large dihedral angles of approximately 80° between the PXZ donors and adjacent benzene rings, which can promote efficient separation of the HOMO and LUMO.²¹⁻²³ As expected, The HOMOs of these emitters are mainly located on PXZ segments due to its good electron-donating and holetransporting properties, while the LUMOs of PXZ-PQM and DPXZ-PQM are localized on the PQM acceptors unit with a slight extent on the phenylene linker, and that of DPXZ-DPPM

Table 1 Photophysical and electrochemical data of PXZ-PQM, DPXZ-PQM, and DPXZ-DPPM

 $\lambda_{\rm PL}$

(nm)a)

592

594

642

 S_1

(eV)^{b)}

2.23

2.25

2.13

 T_1

(eV)^{b)}

2.20

2.23

2.08

is mainly distributed on the DPPM acceptore unite The separated frontier molecular orbitals lead to extremely small theoretical ΔE_{ST} values of 32.5, 2.2, and 41.0 meV for **PXZ**-PQM, DPXZ-PQM and DPXZ-DPPM, respectively, calculated using time-dependent density functional theory (TDDFT) calculation. In comparison with the other two emitters, DPXZ-**PQM** possesses the lowest ΔE_{ST} which accelerates the RISC process from triplet to singlet, indicating that **DPXZ-PQM** may be a better TADF emitter.²⁴⁻²⁷

Thermal Stability and Electrochemical Properties

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under nitrogen atmosphere to study their thermal stabilities. As shown in Fig. S1, DPXZ-PQM and DPXZ-DPPM exhibit a thermal decomposition temperature at 475 and 465 °C at a 5% weight reduction, which is higher than that of **PXZ-PQM** at 368 °C due to larger molecular glass-transition Furthermore. the mass temperature values were observed as 84, 137 and 173 °C for PXZ-PQM, DPXZ-PQM and DPXZ-DPPM, respectively (Fig. S2). These results clearly establish DPXZ-PQM and DPXZ-DPPM more excellent thermal stability compared with PXZ-PQM, indicated that DPXZ-PQM and DPXZ-DPPM can form more stable amorphous film for the OLED fabrication by vacuum deposition.28

Electrochemical properties of these three emitters were carried out by cyclic voltar se three compounds exhibit ble oxidation behavior from the set the oxidation of an а ferrocene/ferrocenium refe ΛO levels of PXZ-PQM, DP are established to be - 5.43/- 3 24 eV, respectively. The HOM ers are almost identical to each nor moieties. Nevertheless, D ЛO energy level relative to PX to increasing the conjugated of nd gaps (E_g) are calculated to b for DPXZ-PQM and 2.25 eV fo all electrochemical data are su ılts reveal that the integration ies has a great effect on the LU

nmetry (0	CV) mea	surements	s. Thes						
ted char	acteristi	cs of re	versibl						
e PXZ don	or. Acco	rding to th	ne onse						
d redu	iction	curves	(vs						
erence) (F	ig. S3), †	the HOMO)/LUMO						
PXZ-PQM	and	DPXZ-DPP	M ar						
.04, - 5.4	6/- 3.09,	and - 5.4	9/- 3.2						
IO energy	/ levels	of these of	emitter						
other, due to their identical dono									
PXZ-DPPI	M has	a deeper	LUMO						
Z-PQM	and DP)	(Z-PQM o	wing to						
degree of the acceptor. Their ban									
e 2.39 eV	for PXZ	-PQM , 2.3	7 eV fo						
r DPXZ-D	PPM, re	spectively	, and a						
Immarized in Table 1. These result									
of two kinds of acceptor moietie									
MO level. ²⁹									
F	DI OV								
E_{g}	PLQY	$\tau_{\rm P}$	$\tau_{\rm d}$						
(ev)	(%)	(ns) ⁵	(µs) ⁵						
2.39	70	21.8	5.37						
2.37	88	38.7	3.77						
2.25	61	25.6	3.53						
$= S_1 - T_1$. ^{d)} Measured from the oxidation an									
			-						

^{a)}Measured in toluene (1imes10⁻⁵ M) at room temperature. ^{b)}The lowest excited singlet (S₁) and triplet (T₁) energies. ^{c)} Δ E_{st} and reduction potential in DCM and DMF solution by cyclic voltammetry. e)Band gap energy. f)Photoluminescence quantum yield in doped film. g)PL lifetimes of prompt fluorescence ($\tau_{\rm p}$) and delayed fluorescence ($\tau_{\rm d}$) for the 5 wt% doped films at 300 K.

 $\Delta E_{\rm ST}$

(eV)c)

0.03

0.02

0.05

HOMO

(eV)d)

-5.43

-5.46

-5.49

LUMO

(eV)d)

-3.04

-3.09

-3.24

 λ_{abs}

(nm)a)

326, 440

325, 432

381, 494

Emitter

PXZ-POM

DPXZ-PQM

DPXZ-DPPM



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Fig. 3 (a) Normalized UV-vis absorption and fluorescence spectra of PXZ-PQM, DPXZ-PQM and DPXZ-DPPM in toluene at room temperature. (b) The temperature-dependent transient PL decays of 5 wt% PXZ-PQM, DPXZ-PQM and DPXZ-DPPM doped in DCzDPy films measured at 100–300 K.

Photophysical Properties

Ultraviolet-visible (UV) absorption and photoluminescence (PL) spectra of these three emitters in dilute toluene solvent (10-5 M) are shown in Fig. 3a and their key photophysical data are summarized in Table 1. PXZ-PQM, DPXZ-PQM and DPXZ-**DPPM** show weak and broad absorption bands absorption maxima at 440, 432 and 494 nm, which can be attributed to the intramolecular charge-transfer (ICT) transition from the PXZ donor to the acceptor cores. And the intense high-energy absorption bands with peaks at 326, 325 and 381 nm can be assigned to the $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions of PXZ and acceptor

cores, respectively. In comparison with PXZ-PQM and DPXZ-PQM, DPXZ-DPPM exhibits significantly red-shifted absorption maxima, which can be ascribed to the increased conjugated degree. The PL spectra of PXZ-PQM and DPXZ-PQM in dilute toluene solution are almost identical with the maximum emission wavelength at 592 and 594 nm, which is a result of cooperation of conjugation effect and charge transfer effect. DPXZ-DPPM shows a large red-shift of 50 nm with an emission peak at 642 nm, suggesting more obvious ICT effect owing to the enhanced acceptor ability.8, 30 The fluorescence and phosphorescence spectra of three emitters were recorded in

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Fig. 4 (a) Device diagram and chemical structures of the materials used for the devices. (b) External quantum efficiency versus current density characteristics. The inset figure shows EL spectra of the devices. (c) Power efficiency and current efficiency versus current density characteristics.

toluene solution at 77 K, respectively, and the singlet (S1) and triplet (T₁) levels were estimated from the onsets of the fluorescence and phosphorescence spectra. As shown in Fig. S4a-S4c, the phosphorescence spectra of these compounds are broad and structureless, illustrating that the phosphorescence derives from the charge transfer (CT) state radiation transition of the triplet excitons. The S_1 and T_1 energy levels are calculated to be 2.23 and 2.20 eV for PXZ-PQM, 2.25 and 2.23 eV for DPXZ-PQM, and 2.01 and 2.06 eV for DPXZ-DPPM. Therefore, ΔE_{ST} s of **PXZ-PQM**, **DPXZ-PQM** and **DPXZ-DPPM** are determined to be 0.03, 0.02 and -0.05 eV, respectively, which are basically consistent with the results of the theoretical calculations. The negative ΔE_{ST} value for **DPXZ-DPPM** originates from the higher triplet excited state (T_n) , which can be explained by the four-level model suggested by Kobayashi et al.³¹ Because the values of S_1 and T_1 determined from the solution could be influenced by the polarity of the solvent, we measured the fluorescence and phosphorescence spectra of **DPXZ-DPPM** in n-hexane at 77 K (Fig. S4d). A positive ΔE_{ST} of 0.05 eV is obtained for **DPXZ-DPPM**. Such small ΔE_{ST} s demonstrate that efficient RISC process from T₁ to S₁ and high triplet exciton utilization can be expected.²⁴

The solid state photophysical properties of three molecules were prepared and investigated by doping 5 wt% emitters in DCzDPy (5,5'-bis(carbazol-9-yl)-3,3'-bipyridine)). The absorption, fluorescence (298 K) and phosphorescence (77 K) spectra of DCzDPy were shown in Fig. S5. As described in Fig. S6, the PL spectra of **PXZ-PQM**, **DPXZ-PQM** and **DPXZ-DPPM**

doped films give broad orange-red to red emission peaking at 588, 586, and 630 nm, respectively, and corresponding photoluminescence quantum yields (PLQYs) of 70%, 88%, and 61%. To get better insight into the TADF natures of these materials, the transient PL decay characters of their doped films were performed. As shown in Fig. S7, PXZ-PQM, DPXZ-PQM and DPXZ-DPPM exhibit two component emission decay profile containing a nanosecond-scale fluorescence prompt component (τ_P) of 21.8, 38.7, and 25.6 ns, and a microsecondscale delayed component (τ_d) of 5.37, 3.77, and 3.53 μ s, respectively. These results are distinctly shorter than the most of reported orange-red/red TADF emitters.^{14-17, 32} We also measured the temperature-dependent transient PL decays of the blend films from 100 K to 300 K (Fig. 3b-d). The results showed that the contributions of delayed components to the PLQY gradually increased with the increase of the temperature, indicating their typical TADF natures of these emitters (Table S2).³³⁻³⁶ Moreover, the related photophysical rate constants of these doped films are calculated according to Equation S1–S6, and the detailed data are summarized in Table S3. Profiting from highly rigid molecular structures, the rate constants of fluorescent ($k_{\rm F}$) values of these TADF emitters in the range of 10⁷ s⁻¹, which are much higher than most of the reported TADF emitters.³⁷⁻³⁹ Their rate constants of RISC (k_{RISC}) are estimated to be 0.91×10^5 , 2.05×10^5 and 1.8×10^5 s⁻¹, respectively. The highest PLQY and the maximum k_{RISC} confirm that DPXZ-PQM may realize best EL performance among them.

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able 2 Summarized device performance	s of the devices based on PXZ-PQ	M, DPXZ-PQM, and DPXZ-DPPM.
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Emitter	V _{on} (V) ^{a)}	L_{max} (cd m ⁻²) ^{b)}	CE (cd A ⁻¹) ^{c)}	PE (lm W ⁻¹) ^d)	EQE (%) ^e	$\lambda_{\rm EL}$ (nm) ^f	CIE (x, y) ^g	
PXZ-PQM	3.4	21900	45.2	37.7	20.4, 17.5, 11.3	592	(0.53, 0.46)	
DPXZ-PQM	2.8	14140	60.7	67.4	26.0, 20.1, 13.7	590	(0.51, 0.48)	
DPXZ-DPPM	3.6	6017	13.6	10.6	11.5, 10.5, 6.8	630	(0.61, 0.38)	

^{a)}Turn-on voltage at 1 cd m⁻². ^{b)}Maximum luminance. ^{c)}Maximum current efficiency. ^{d)}Maximum power efficiency. ^{e)}Maximum EQE, and values at 100 and 1000 cd m⁻². ^{f)}The wavelength of the EL peak at 100 cd m⁻². ^{g)} CIE (x,y): CIE coordinates measured at 100 cd m⁻².

Electroluminescent Properties

To investigate the EL properties of these TADF materials, multilayer devices were fabricated using PXZ-PQM, DPXZ-PQM and **DPXZ-DPPM** doped in DCzDPy as the emitters, respectively, with the following optimized device structure: ITO/TAPC (45 nm) /TCTA (10 nm)/DCzDPy: dopant (5 wt%) (20 nm)/B3PymPm (50 nm)/LiF (1 nm)/Al (100nm), where ITO (indium tin oxide), LiF and Al are used as the anode, the electron-injecting layer and the cathode, respectively; TAPC (1,1-bis[4-[N,N-di(p-tolyl)-amino]phenyl]cyclohexane) and B3PymPm (4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2methylpyrimidine)) are used as the hole-transporting layer and electron-transporting layer, respectively; TCTA (4,4',4"tris(carbazol-9-yi)triphenylamine) acts as the electron-blocking layer. The chemical structures and energy level diagram of the materials used as well as the device architectures of the devices are shown in Fig. S8 and 4a. The current densityvoltage-luminance (J-V-L) characteristics, EL spectra and efficiency versus luminance curves are shown in Fig. S9, 4b and c, and the device performance parameters are summarized in Table 2.

As presented in Fig. S9, the turn-on voltages of PXZ-PQM, DPXZ-PQM, and DPXZ-DPPM based devices are 3.4, 2.8 and 3.6 V, respectively. The PXZ-PQM-, DPXZ-PQM-, and DPXZ-DPPM-based devices display orange-red to red emission with peaks at 592, 590, and 630 nm, respectively, corresponding to the Commission Internationale de L'Eclairage (CIE) coordinates of (0.53, 0.46), (0.51, 0.48) and (0.61, 0.38). The DPXZ-DPPMbased device shows a maximum current efficiency (CE_{max}) of 13.6 cd A⁻¹, a maximum power efficiency (PE_{max}) of 10.6 lm W⁻¹ and a maximum external quantum efficiency (EQE_{max}) of 11.5%. Furthermore, the PXZ-PQM-based device displays higher efficiencies of 45.2 cd A⁻¹, 37.7 lm W⁻¹ and of 20.4%, which may be ascribed to the higher PLQY of PXZ-PQM. Encouragingly, the DPXZ-PQM-based device achieves the best EL performance with CE_{max} of 60.7 cd A⁻¹, PE_{max} of 67.4 Im W⁻¹ and EQE_{max} of 26.0%. Fig. 5 shows the device performances of reported orange-red to red TADF-OLEDs with emission maxima at 580-650 nm. Obviously, a state-of-the-art EQE of 26.0% is among the highest values for TADF-OLEDs emitting in orangered to red range without any light out-coupling enhancement.5, 7, 14-17, 32, 39-45 Compared with PXZ-PQM and DPXZ-DPPM, more superior performance of the DPXZ-PQMbased device can be attributed to the highest PLQY, a relatively

small ΔE_{sT} value and the maximum k_{RISC} of **DPXZ-PQM**. More importantly, these three devices exhibit a mild efficiency rolloff feature. At a luminance of 100 and 1000 cd m⁻², the EQE values still maintain to be a high level of 17.5 and 11.3% (roll off: 14.2 and 44.6%) for the **PXZ-PQM**-based device, 20.1 and 13.7% (roll off: 22.7 and 47.3%) for the **DPXZ-PQM**-based device, 10.5 and 6.7% (roll off: 8.7 and 40.9%) for the **DPXZ-DPPM**-based device, respectively (Table 2). The EQE value of 20.1% is also among the best device performance reported for orange-red/red TADF-OLEDs at a luminance of 100 cd m⁻².⁴⁰⁻⁴³

In order to manifest their prominent EL performances, the theoretical maximum EQE can be expressed by the following Equation $1:^{46}$

 $EQE = \gamma \times (0.25 \times \Phi_{\rm F} + 0.25 \times \Phi_{\rm TADF} + 0.75 \times \Phi_{\rm TADF} / \Phi_{\rm ISC}) \times \eta_{\rm out}$ (1)

Where γ is the charge recombination factor, which is ideally 100% if holes and electrons are completely recombined to form excitons, $\Phi_{\rm F}$ is the fluorescence efficiency, $\Phi_{\rm TADF}$ is the TADF efficiency, $\Phi_{\rm ISC}$ is the intersystem crossing quantum efficiency, $\eta_{\rm out}$ is the light-out-coupling efficiency. Therefore, the theoretical maximum EQEs of these three devices can be calculated to be 20.9% for **PXZ-PQM**, 26.4% for **DPXZ-PQM** and 17.9% for **DPXZ-DPPM** by assuming $\eta_{\rm out} = 0.3$, respectively, in good agree with their experimental maximum EQE values, implying high exciton utilization up to 98.5% in OLEDs.



6.52.

Fig. 5 The EQEs summary of orange-red to red TADF OLEDs with emission peaks from 580 to 650 nm.

2. Conclusions

In summary, by fusing two weak electron-withdrawing units, the rigid planar PQM and DPPM acceptors were used to constructed orange-red to red TADF emitters. The rigid and planar constituent groups and large steric hindrance between donor and acceptor units endow these emitters high PLQYs and small $\Delta E_{sT}s$. Among them, **DPXZ-PQM** exhibits the highest PLQY as high as 88%, a relatively small ΔE_{ST} of 0.02 eV and the maximum k_{RISC} . As a result, the orange-red TADF doped device based on **DPXZ-PQM** shows an extremely high EQE_{max} of up to 26.0% with a peak at 590 nm, which is among the highest values for orange-red to red TADF-OLEDs without any light out-coupling enhancement. More importantly, a low efficiency roll-off is rendered and the EQEs still maintain 20.1 and 13.7% at a luminance of 100 and 1000 cd m⁻². This study provides a new insight for developing orange-red/red TADF emitters with high PLQY and short τ_{d} .

3. Experimental Section

Synthesis of (2-(4-bromophenyl)quinoxalin-6-yl)phenylmethanone (Br-PQM)

To a mixture of 4-bromophenacyl bromide (1.10 g, 4.0 mmol) and (3,4-diaminophenyl)phenylmethanone (0.93 g, 4.4 mmol) in 30 mL of water and hexadecyltrimethylammonium bromide (CTAB) (0.36 g, 2.5 mmol) were added under nitrogen atmosphere and stirred for 12 hours at 120 °C. Then, the reaction mixture was poured into cold water, and the precipitate was filtered and dried under vacuum. The crude product was purified by column chromatography with dichloromethane as the eluent to obtain a white solid in 57% yield. ¹H NMR (400 MHz, Chloroform-d): δ 9.38 (s, 1H), 8.52 -8.47 (m, 1H), 8.29 - 8.23 (m, 2H), 8.16 - 8.12 (m, 2H), 7.93 -7.88 (m, 2H), 7.75 - 7.71 (m, 2H), 7.69 - 7.62 (m, 1H), 7.57 -7.52 (m, 2H). ¹³C NMR (101 MHz, Chloroform-d): δ 195.57, 152.12, 144.05, 143.86, 140.75, 138.13, 137.08, 135.09, 132.98, 132.54, 132.32, 130.48, 130.19, 130.07, 129.21, 128.60, 125.77. EIMS m/z: 388.16[M]⁺. Anal. calcd for C₂₁H₁₃BrN₂O: C 64.80, H 3.37, Br 20.53, N 7.20, O 4.10; found: C 64.60, H 3.48, Br 20.60, N 7.21, O 4.11.

Synthesis of (2-(4-(phenoxazin-10-yl)phenyl)quinoxalin-6yl)phenylmethanone (PXZ-PQM)

Br-PQM (0.97 g, 2.5 mmol), phenoxazine (0.51 g, 2.8 mmol), sodium tert-butoxide (0.48 g, 5.0 mmol) were combined in a 250 mL flask and cycled under nitrogen and vacuum three times, before tris(dibenzylideneacetone)dipalladium (0.10 g, 0.1 mmol), 2.5 mL of a 1.0 M solution of tri-tertbutyl phosphine in toluene, and 50.0 mL of o-xylene were added. The reaction was performed for 12 hours at 140 °C, water (25 mL) was added to quench the reaction, the mixture was then extracted with dichloromethane. The organic solution was ARTICLE

dried over anhydrous sodium sulfate. The crude product was purified using column chPomatography^{C05}with bv dichloromethane as the eluent to obtain an orange solid in 73% yield. ¹H NMR (500 MHz, Chloroform-*d*): δ 9.48 (s, 1H), 8.54 (t, J = 1.3 Hz, 1H), 8.50 - 8.46 (m, 2H), 8.31 (d, J = 1.2 Hz, 2H), 7.97 - 7.87 (m, 2H), 7.69 - 7.64 (m, 1H), 7.63 - 7.59 (m, 2H), 7.56 (m, J = 7.7 Hz, 2H), 6.74 (dd, J = 7.8, 1.6 Hz, 2H), 6.69 (t, J = 7.5 Hz, 2H), 6.63 (td, J = 7.6, 1.7 Hz, 2H), 6.05 (dd, J = 8.0, 1.5 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 195.62, 152.40, 144.26, 144.13, 144.03, 141.60, 140.85, 138.32, 137.09, 136.40, 133.99, 133.04, 132.36, 131.89, 130.60, 130.54, 130.23, 130.18, 128.64, 123.36, 121.77, 115.72, 113.36. EIMS m/z: 491.38[M]*. Anal. calcd for C₃₃H₂₁N₃O₂: C 80.64, H 4.31, N 8.55, O 6.50; found: C 80.56, H 4.31, N 8.61, O

Synthesis of (2,3-bis(4-bromophenyl)quinoxalin-6yl)phenylmethanone (DBr-PQM)

A suspension of 1,2-bis(4-bromophenyl)ethane-1,2-dione (1.10 g, 3.0 mmol) and (3,4-diaminophenyl)phenylmethanone (0.64 g, 3.0 mmol) in acetic acid (20 mL) was heated to reflux for 8 hours. After cooled to room temperature, poured the resulting mixture into ice-water (200 mL), and then filtered. The solid was washed with water several times. The crude product was purified by column chromatography to obtain a light yellow solid in 80% yield. ¹H NMR (400 MHz, Chloroform-d): δ 8.50 (t, J = 1.2 Hz, 1H), 8.27 (t, J = 1.2 Hz, 2H), 7.93 – 7.86 (m, 2H), 7.68 - 7.62 (m, 1H), 7.56 - 7.49 (m, 6H), 7.47 - 7.39 (m, 4H). ¹³C NMR (101 MHz, Chloroform-d): δ 195.68, 153.63, 153.10, 142.96, 140.28, 138.76, 137.27, 137.24, 137.09, 133.00, 132.34, 131.86, 131.52, 131.40, 130.34, 130.19, 129.76, 128.62, 124.34, 124.17. EIMS m/z: 543.76[M]⁺. Anal. calcd for C₂₇H₁₆Br₂N₂O: C 59.59, H 2.96, Br 29.36, N 5.15, O 2.94; found: C 59.48, H 2.99, Br 29.43, N 5.19, O 2.91.

Synthesis of (2,3-bis(4-(phenoxazin-10-yl)phenyl)quinoxalin-6yl)(phenyl)methanone (DPXZ-PQM)

According to the procedure similar to that of PXZ-PQM, compound DPXZ-PQM was synthesized using DBr-PQM (1.09 g, 2.0 mmol) to obtain an orange-red solid in 81% yield. ¹H NMR (500 MHz, Chloroform-d): δ 8.61 (d, J = 1.6 Hz, 1H), 8.39 – 8.33 (m, 2H), 7.96 – 7.92 (m, 2H), 7.85 – 7.77 (m, 4H), 7.69 – 7.65 (m, 1H), 7.56 (t, J = 7.7 Hz, 2H), 7.44 - 7.37 (m, 4H), 6.70 (ddd, J = 7.9, 4.4, 1.4 Hz, 4H), 6.63 (m, J = 7.8 Hz, 4H), 6.52 (qd, J = 7.7, 1.5 Hz, 4H), 5.95 (t, J = 8.8 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-d): δ 195.68, 154.31, 143.98, 143.14, 140.46, 140.37, 140.25, 139.01, 138.62, 137.08, 133.89, 133.07, 132.71, 132.71, 132.59, 132.45, 131.09, 130.21, 128.67, 123.46, 121.73, 115.68, 113.17. EIMS m/z: 748.42[M]⁺. Anal. calcd for C₅₁H₃₂N₄O₃: C 81.80, H 4.31, N 7.48, O 6.41; found: C 81.71, H 4.33, N 7.49, O 6.47.

Synthesis of (3,6-dibromodibenzophenazin-11yl)phenylmethanone (DBr-DPPM)

According to the procedure similar to that of DBr-PQM, compound DBr-DPPM was synthesized using 3.6dibromophenanthrene-9,10-dione (0.64 g, 6.0 mmol) to obtain a red solid in 83% yield. ¹H NMR (400 MHz, Chloroform-d): δ 9.13 (d, J = 8.6 Hz, 1H), 9.05 (d, J = 8.6 Hz, 1H), 8.59 (d, J = 1.2 Hz, 1H), 8.46 (d, J = 2.3 Hz, 2H), 8.35 – 8.32 (m, 2H), 7.98 – 7.95 (m, 2H), 7.79 (ddd, J = 12.9, 8.7, 1.9 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.62 – 7.57 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 195.77, 143.73, 142.73, 142.36, 141.17, 138.39, 137.23, 132.97, 132.78, 132.54, 132.25, 131.82, 130.23, 129.93, 128.93, 128.64, 128.35, 128.06, 126.26, 125.99. EIMS *m/z*: 541.73[M]⁺. Anal. calcd for C₂₇H₁₄Br₂N₂O: C 59.81, H 2.60, Br 29.47, N 5.17, O 2.95; found: C 59.73, H 2.62, Br 29.51, N 5.22, O 2.92.

Synthesis of (3,6-di(phenoxazin-10-yl)dibenzophenazin-11yl)phenylmethanone (DPXZ-DPPM)

According to the procedure similar to that of PXZ-PQM, compound DPXZ-DPPM was synthesized using DBr-DPPM (1.08 g, 2.0 mmol) to obtain a red solid in 84% yield. ¹H NMR (500 MHz, Chloroform-*d*): δ 9.75 (dd, *J* = 8.6, 2.1 Hz, 1H), 9.67 (dd, *J* = 8.6, 2.1 Hz, 1H), 8.78 (s, 1H), 8.54 (dd, *J* = 8.9, 2.4 Hz, 3H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.81 (dd, *J* = 19.7, 8.5 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 2H), 6.76 (t, *J* = 6.2 Hz, 4H), 6.69 (q, *J* = 6.9 Hz, 4H), 6.61 (q, *J* = 7.0 Hz, 4H), 6.06 (t, *J* = 9.3 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 195.80, 144.02, 143.23, 142.86, 141.99, 141.78, 141.47, 138.63, 137.23, 134.49, 134.20, 134.02, 133.07, 132.93, 131.30, 130.30, 130.13, 130.06, 129.81, 128.70, 125.96, 123.38, 121.88, 121.86, 115.79, 113.34. EIMS *m/z*: 746.46[M]⁺. Anal. calcd for C₅₁H₃₀N₄O₃: C 82.02, H 4.05, N 7.50, O 6.43; found: C 81.90, H 4.11, N 7.55, O 6.44.

Conflicts of interest

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The authors declare no competing financial interests.

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Graphical Abstract

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A class of novel donor-acceptor orange-red to red thermally activated delayed fluorescence (TADF) emitters with the maximum external quantum efficiency (EQE) up to 26.0% and extremely low efficiency roll-off have been designed and synthesized.