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Considerable efforts have been devoted to the development of highly efficient blue light-emitting materials. However, deep-blue fluorescence materials that can satisfy the Commission Internationale de l'Eclairage (CIE) coordinates of (0.14, 0.08) of the National Television System Committee (NTSC) standard blue and, moreover, possess a high external quantum efficiency (EQE) over 5%, remain scarce. Here, the unusual luminescence properties of triphenylaminebearing 2-(2'-hydroxyphenyl)oxazoles (3a-3c) and their applications in organic light-emitting diodes (OLEDs) are reported as highly efficient deep-blue emitters. The 3a-based device exhibits a high spectral stability and an excellent color purity with a narrow full-width at half-maximum of 53 nm and the CIE coordinates of (0.15, 0.08), which is very close to the NTSC standard blue. The exciton utilization of the device closes to 100%, exceeding the theoretical limit of 25% in conventional fluorescent OLEDs. Experimental data and theoretical calculations demonstrate that 3a possesses a highly hybridized local and charge-transfer excited state character. In OLEDs, 3a exhibits a maximum luminance of 9054 cd m⁻² and an EQE up to 7.1%, which is the first example of highly efficient blue OLEDs based on the sole enol-form emission of 2-(2'-hydroxyphenyl)azoles.

1. Introduction

Excited-state intramolecular proton transfer (ESIPT) materials have received much attention due to their applications in

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fluorescence probes, optical memory, proton transfer lasers, and organic light-emitting diodes (OLEDs).^[1,2] 2-(2'-Hydroxyphenyl)azoles, a kind of typical ESIPT molecules, exist exclusively as an enol form (E) in the ground state. Upon excitation, the phenyl hydroxyl proton is transferred from the oxygen atom to the nitrogen atom of azole via the intramolecular hydrogen bond (H-bond), resulting in an isomerization from the excited enol form (E*) to the excited keto form (K*).^[1b,c] The formation of intramolecular H-bond is an essential prerequisite for the efficient ESIPT process, since the proton transfer takes place along the locus of intramolecular H-bond. Polar or protic solvents can form an intermolecular H-bond with the proton donor or acceptor of ESIPT molecules, which could suppress the generation of the intramolecular H-bond.^[1b,c] Therefore, 2-(2'-hydroxyphenyl)azoles generally exhibit only the ESIPT keto-form emission

in hydrocarbon and nonpolar solvents, while the dual emission of the excited enol and keto forms can be observed in polar and protic solvents. In the solid solution, such as in poly(methyl methacrylate) and polystyrene (PS) films, the photoluminescence (PL) spectra of 2-(2'-hydroxyphenyl)azoles as well as their electroluminescence (EL) spectra in OLEDs are usually similar to those in nonpolar solvent, which typically show a keto-form emission.^[1b-d] Although the electron-donating or electronaccepting groups on the azole could significantly affect the keto-form emission peak position and its intensity,[1b] the examples of the complete suppression of the keto-form emission of 2-(2'-hydroxyphenyl)azoles in OLEDs have not been described yet. Recently, we unexpectedly discovered that the introduction of an electron-donating triphenylamine (TPA) group into the side of azole can lead to a sole enol-form emission in PL spectra, and the ESIPT keto-form emission is suppressed completely. Moreover, due to the lack of keto-form emission at the long wavelength region, these compounds not only show a blue emission at the short wavelength region, but also possess a high fluorescence quantum efficiency in both solution and PS film, which predicts potential high-efficiency blue OLEDs.

Blue OLEDs play a pivotal role in the realization of fullcolor display.^[3] Developing efficient blue EL emitters remains



a huge challenge due to the intrinsic wide band gap of blue emitting materials, which makes it difficult to inject charges into emitters.^[3b] The high-efficiency blue OLEDs mainly utilize phosphorescent metal complexes as the emission layer.^[4] However, the use of expensive rare metals, mainly involving iridium (Ir) and platinum (Pt), limits their practical applications, let alone difficult synthesis of metal complexes, complicated device fabrication, instability, degradation, and serious roll-off in devices at high brightness.^[5] Moreover, the most widely used blue phosphorescent material, FIrpic, is a sky-blue emitter with the Commission Internationale de l'Eclairage (CIE) coordinates of (0.16, 0.29).^[6] Therefore, it is very necessary to explore highly efficient deep-blue fluorescent emitters.

In recent years, considerable efforts have been devoted to developing highly efficient deep-blue fluorescence materials.^[3,7] However, efficient deep-blue light-emitting materials, which can satisfy the National Television System Committee (NTSC) standard blue CIE coordinates of (0.14, 0.08), are rare, and especially, deep blue emitters with high current efficiency (CE) and external quantum efficiency (EQE) are more scarce.^[7] To date, no reports of efficient deep-blue OLEDs based on 2-(2'-hydroxyphenyl)azoles are available, except a 2-(2'-hydroxyphenyl)imidazole derivative with the CIE coordinates of (0.15, 0.11) and a maximum EQE of 2.94% reported by Park et al.^[2c] In this

work, we will focus on the investigation of unusual luminescence properties of TPA-bearing 2-(2'-hydroxyphenyl)oxazoles and their promising applications in highly efficient deep-blue OLEDs.

2. Results and Discussions

2.1. Synthesis, Characterization, and Photoluminescence

2.1.1. Synthesis of 2-(2'-Hydroxyphenyl)oxazoles

Based on the rhodium-catalyzed internally oxidative C–H/C–H cross-coupling reaction between phenols and azoles developed previously by us,^[8] the highly efficient and concise synthetic routes to 2-(2'-hydroxyphenyl)oxazoles **3a–3c** are shown in **Scheme 1**. First, *N*-aryloxyamines were obtained by the reaction of potassium phenoxide with *O*-(mesitylsulfonyl)hydroxylamine as the aminating reagent or by the copper-mediated cross-coupling of (4-(trifluoromethyl)phenyl)boronic acid with *N*-hydroxyphthalimide and followed hydrazinolysis.^[9] Next, the *N*-acetylation of *N*-aryloxyamines with acetyl chloride gave *N*-aryloxyacetamides **1** in acceptable yields.^[9d] The palladium-catalyzed Suzuki cross-coupling of arylboronic acid with 5-(4'-bromophenyl)oxazole delivered **2** in an excellent



Scheme 1. Synthetic routes of 3a-3c. XPhos: 2-(dicyclohexylphosphino)-2',4',6'-triisopropylbiphenyl.



yield.^[9c] Finally, 2-(2'-hydroxyphenyl)oxazoles 3a-3c were synthesized using the rhodium-catalyzed internally oxidative C-H/C-H cross-coupling reaction of *N*-aryloxyacetamide 1 with 2 through dual C-H activation. Their structures were confirmed by NMR, high resolution mass spectra (HRMS), and single crystal X-ray diffraction. Using the similar synthetic method, 2-(2'-hydroxyphenyl)-5-phenyloxazole (HPO) was also prepared as a reference compound (Section III, Supporting Information).

2.1.2. Absorption and Emission Properties

The UV-vis absorption spectra of compounds 3a-3c and HPO were recorded in toluene and PS film at room temperature (Figure S1, Supporting Information), and their absorption maxima are summarized in Table 1. For HPO, the lower absorption band at 300 nm corresponds to the π - π * transition of 5-phenyloxazole, while another intense absorption band at 330 nm is assigned to the coupling between 5-phenyloxazole and the hydroxyphenyl ring.^[1b,10] There is an absorption shoulder at 346 nm, which may be a vibrational structure.^[10e] Compared to HPO, the two absorption bands of 3a-3c at the short wavelength region are red-shifted slightly, and an additional absorption band at the long wavelength region appears at around 370 nm (Figure S1a, Supporting Information), which is assigned to a charge-transfer (CT) transition from TPA to azole. The CT band of 3a-3c essentially overlaps with the absorption band of the π - π * transition of 2-(2'-hydroxyphenyl)-5-phenyloxazole moiety. Thus, the latter as absorption shoulders appear at around 334 and 339 nm for 3a and 3c, respectively (Figure S1a, Supporting Information). For 3b, the absorption shoulder is not observed, which may be due to the electron-donating effect of the methyl substituent on the phenolic ring. The absorption spectra of 3a-3c and HPO in PS film are almost consistent with those in toluene (Figure S1b, Supporting Information).

Most 2-(2'-hydroxyphenyl)azoles such as 2-(2'-hydroxyphenyl)benzimidazole (λ_{em} : 469 nm, in cyclohexane), 2-(2'-hydroxyphenyl)benzothiazole (λ_{em} : 525 nm, in hexane), and 2-(2'-hydroxyphenyl)benzoxazole (λ_{em} : 500 nm, in hexane), only exhibit the ESIPT keto-form emission in nonpolar and low polarity solvents.^[1b,10a,c,11] The emission spectrum of **HPO** is consistent with those of these typical 2-(2'-hydroxyphenyl)-azoles, which shows a sole keto-form emission at 475 nm in toluene (**Figure 1**a and Table 1). However, compounds **3a**, **3b**, and **3c** in toluene solution only exhibit the sole enol-form emission at 420, 420, and 432 nm, respectively (Figure 1a and

Table 1. Absorption and emission maxima of 3a-3c and HPO.

Compounds ^{a)}	In to	luene	In PS films		
	$\lambda_{ m abs}$ [nm]	$\lambda_{ m em}$ [nm]	λ_{abs} [nm]	$\lambda_{ m em}$ [nm]	
3a	368	420	370	444	
3b	370	420	370	447	
3c	372	432	373	450	
HPO	330	475	331	489	

 $^{a)}Absorption$ and emission maxima were measured in toluene (5.0 \times 10 $^{-5}$ M) and PS film (5.0 wt%).



Figure 1. Normalized emission spectra of **3a–3c** and 2-(2'-hydroxy-phenyl)-5-phenyl-oxazole (**HPO**) in a) toluene (5.0×10^{-5} M) and b) PS film (c = 5.0 wt%).

Table 1). The substituent on the phenolic ring, whether it is electron-donating methyl (**3b**) or electron-withdrawing trifluoromethyl (**3c**), shows a small effect on the emission spectrum. The enol-form emissions of 3a-3c are located in the blue spectral range, while the ESIPT keto-tautomer emissions were not observed in both toluene solution and PS film (Figure 1 and Table 1), which are distinctly different from HPO as well as most of the existing 2-(2'-hydroxyphenyl)azoles, and thus are rather unusual.

2.1.3. Crystal Structure

To confirm whether the absence of intramolecular H-bond causes the sole enol-form emission, 3a was chosen as a representative example, and its single crystals were obtained by slow diffusion of petroleum ether into methylene dichloride solution. The crystal structure of 3a is shown in Figure S18 (Supporting Information), and the key crystallographic data



are summarized in Table S10 (Supporting Information). The crystallography data of 3a clearly indicate the presence of intramolecular H-bond between the phenyl hydroxyl proton and the oxazole nitrogen atom with a distance of 1.938 Å. Moreover, the 2-(2'-hydroxyphenyl)oxazole moiety is almost coplanar due to the fixation of H-bond. The dihedral angle of the central biphenyl is 31.9° (θ_3). As for the twisted TPA moiety resembling propeller blades, the dihedral angles between the phenyl ring as a linker and the other two phenyl rings are 66.65° (θ_4) and 60.88° (θ_5), respectively. The presence of intramolecular H-bond is further confirmed by ¹H NMR data. In CDCl₃, the phenyl hydroxyl proton resonance signal appears at δ 11.18 ppm (Figure S19, Supporting Information), which is consistent with the large downfield shift ($\delta > 10$ ppm) of the phenyl hydroxyl proton in most ESIPT molecules possessing a strong intramolecular hydrogen bond.^[2f]

2.1.4. Solvatochromic Effects

The solvent polarity-dependent emission behavior of 3a was studied using the Lippert-Mataga model.^[12] The absorption spectra of 3a shows a slight change within the scope of 10 nm as the solvent polarity increases, indicating a negligible dipolar change in the ground state with the change of solvent polarity. Its emission spectra present a remarkable red shift with the increase of the solvent polarity: from 406 nm in nonpolar hexane to 481 nm in polar acetonitrile, indicating a typical CT character in the excited state (Figure 2a and Table S1, Supporting Information).^[13] In contrast, HPO exhibits solely the keto-form emission in nonpolar and low polarity solvents, but in conjunction with a weak emission of enol form in highly polar solvents (Figure S3 and Table S2, Supporting Information). As shown in Figure 2c, the keto emission of HPO seems to be solvent-independent, whereas its enol emission exhibits a slightly bathochromic shift of 7 nm (from 375 to 382 nm) with increasing solvent polarity, which is in accordance with the characteristics of the typical ESIPT molecules.^[1]

The dipole moment change between the excited state and ground state ($\Delta \mu = \mu_e - \mu_g$) can be estimated by the slope of the fitted line of the Stokes shift in different solvents versus the corresponding solvent polarity parameters.^[12] Notably, **3a** exhibits only one slope of 10 956 (r = 0.98), and the $\Delta \mu$ value is calculated to be 14.4 D (Figure 2b, and see Section V, Supporting Information),^[14] which is different from a negligible solvatochromism of **HPO**. Such a large $\Delta \mu$ value of **3a** clearly illustrates a considerable contribution of intramolecular charge-transfer (ICT) character in the excited state.^[14]

2.1.5. ICT/ESIPT Mechanism

The ESIPT and ICT processes of organic dyes are usually coupled together.^[1a-c] A proposed ICT/ESIPT mechanism of **3a** is shown in **Scheme 2**. Solvatochromic experiments have shown that ultrafast ICT reaction takes place upon photoexcitation, generating the ICT state (**I**), which can be stabilized by delocalization energy of ICT-induced transient push-pull structure.





Figure 2. a) Normalized emission spectra of 3a in different solvents (concentration: 5×10^{-5} M). Linear fitting of Lippert–Mataga model of b) 3a and c) HPO.

In contrast, the energy level of conformer (II) is relatively higher due to the lack of the delocalization energy of push-pull effects, which leads to a high energy barrier for isomerization from enol form (I) to keto form (II). Theoretical calculations

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Scheme 2. The ICT/ESIPT mechanism of 3a.

further provide a supplementary support for this deduction. The enol-form species of the ground-state **HPO** and **3a** are dominant because their energies are lower than those of the keto-forms by 11.65 and 11.72 kcal mol⁻¹, respectively (**Figure 3** and Table S3, Supporting Information). In the lowest excited state (S₁), the energy level of the keto-form of **HPO** is lower than that of the enol form by 1.09 kcal mol⁻¹, while it is higher by 6.41 kcal mol⁻¹ for **3a**. Therefore, the enol form of **HPO** is prone to transferring to the keto form in the excited state, whereas the transformation of **3a** from the excited-state enol to keto is a significantly endergonic process, which indicates that the thermodynamic equilibrium favors the enol species, thus resulting in the lack of keto-form emission. Furthermore, time-resolved PL experiments revealed a monoexponential decay of the excited state for **3a** in different solvents (Figure S4 and



Figure 3. Diagrams of the ESIPT processes and calculated energy levels of $\ensuremath{\text{HPO}}$ and $\ensuremath{\textbf{3a}}.$

Table S4, Supporting Information), indicating only a single emission species.

2.1.6. Photoluminescence Efficiencies and CIE Coordinates

As seen from Table 2, 3a exhibits high fluorescence quantum efficiency in various solvents with different polarities (74%–99%) as well as in PS film (41%) (Table S1, Supporting Information). It is presumed that the introduction of propeller-like TPA into the 2-(2'-hydroxyphenyl)azole skeleton would restrain the molecular aggregation, which may endow them with a strong emission. Moreover, an intramolecular H-bond would restrict the relative rotation of the linkage between phenol and oxazole, which may reduce the possible energy loss through the nonradiative rotational relaxation. In general, bridged-model conjugated molecules in which the intramolecular rotation is blocked, such as fluorene and its derivatives, exhibit higher fluorescence quantum yields than the corresponding unbridged compounds, such as biphenyl derivatives.^[15] The intramolecular H-bond of 2-(2'-hydroxyphenyl)azoles may be considered as a special type of noncovalently bridged model, but it has seldom been studied as a bridged model to lock molecular conformation and thus enhance emission intensity, because the typical 2-(2'-hydroxyphenyl)azoles usually tend to undergo the ESIPT reaction.^[1]

The 2-(2'-hydroxyphenyl)azoles with the ESIPT characteristics have been widely studied as blue emitting materials.^[1b] However, most ESIPT molecules exhibit relatively low fluorescence quantum efficiency due to the presence of various nonradiative deactivation pathways of the keto-form excited state.^[1b] For example, **HPO** shows low fluorescence quantum efficiency of from 0.45 in toluene to 0.10 in acetonitrile (Table 2 and

Table 2. Fluorescence quantum yields and CIE₁₉₃₁ of **3a–3c** and **HPO**.

Compounds ^{a)}	In toluene		In PS films		
	Φ_{f} [%] CIE ₁₉₃₁		Φ_f [%]	CIE ₁₉₃₁	
3a	88	(0.15, 0.05)	41	(0.15, 0.11)	
3b	86	(0.15, 0.05)	41	(0.15, 0.13)	
3c	84	(0.15, 0.07)	40	(0.15, 0.11)	
НРО	45	(0.16, 0.31)	<1	(0.19, 0.37)	

^{a)}Absolute quantum yield (Φ_{f}) and CIE₁₉₃₁ were measured in toluene (5.0 × 10⁻⁵ м) and PS film (5.0 wt%).

Table S2, Supporting Information). In PS film, its quantum yield is even lower than 0.01. In contrast, **3a–3c** exhibit remarkably high fluorescence quantum yields in toluene solution (84%–88%) and in PS films (40%–41%). The molecular pixel behaviors of **3a–3c** were also evaluated by reproducing colors in the CIE₁₉₃₁ XYZ color space and the xy chromaticity diagram. All three compounds exhibit bright deep-blue emissions in both toluene solution and PS film (Table 2 and Figure S5, Supporting Information), which show great promise for applications in high-performance blue OLEDs.

2.1.7. Thermal Properties

The thermal properties of **3a** were studied by thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC). TGA measurement demonstrates that **3a** is a highly thermally stable material. Its thermal-decomposition temperature (T_d) at 5% weight loss is 373 °C. DSC measurement, performed in the temperature range from 20 to 200 °C, shows that **3a** melts at 192 °C. Before the sample completely melts, a rather smooth DSC curve was observed without any glass transition peak or other phase transformation, demonstrating a good morphological stability (Figures S6 and S7, Supporting Information).

2.1.8. Electrochemical Properties

Cyclic voltammetry (CV) was carried out to evaluate the electrochemical properties and energy levels of the 3a-3c and HPO. Compounds 3a-3c show reversible oxidation waves, but HPO only shows an irreversible oxidation wave (Figure S8, Supporting Information). The optical bandgaps are calculated from the absorption onset of their UV-vis spectra in dichloromethane, which are 3.00, 2.99, 2.96, and 3.52 eV for 3a, 3b, 3c, and HPO, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are estimated by CV and optical bandgaps, which are -5.32/-2.32, -5.33/-2.32, -5.30/-2.34, and -5.63/-2.11 eV for 3a, 3b, 3c, and HPO in CH2Cl2, respectively (Table S5, Supporting Information). In comparison with HPO, the HOMO levels of 3a-3c are raised, while the LUMO levels are lowered. Therefore, the absorption bands of **3a-3c** are significantly redshifted compared to HPO. The HOMO levels of 3a-3c are also evaluated by ultraviolet photoelectron spectroscopy spectra, which is in good agreement with the corresponding values determined by CV. The LUMO levels are estimated by subtracting the optical bandgap of the solid films from the HOMO levels. The HOMOs and LUMOs of 3a-3c in solid states were calculated to be -5.35/-2.47, -5.36/-2.50, -5.31/-2.46 eV, respectively (Table S6 and Figure S9, Supporting Information).

2.2. Electroluminescence

2.2.1. Electroluminescence Performances

The EL properties of **3a** in OLED devices were further surveyed. The device configuration fabricated by vacuum deposition

is ITO/MoO₃ (3 nm)/TAPC (50 nm)/3a (x wt%):CBZ₂-F₁ (20 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm). In the devices, MoO₃ and LiF serve as the hole- and electron-injecting materials, respectively. 3a doped in 3,3'-(9H-fluorene-9,9diyl)bis(9-phenyl-9H-carbazole) (CBZ₂-F₁) with an optimized doping level of 13 wt% is used as the emitting layer (For details, see Section X, Supporting Information). TAPC [1,1-bis{(di-4-tolylamino)phenyl}cyclohexane] and TmPyPB [1,3,5-tri(m-pyrid-3-ylphenyl)benzene)] act as the hole- and electron-transporting materials, respectively (Figure S10, Supporting Information). From the EL spectrum of 3a, as shown in Figure 4b, one can see an obvious blue emission with $\lambda_{\rm max}$ at 443 nm, which is consistent with its PL emission in thin film (Figure S13, Supporting Information), indicating that the EL emission is still the enol-form emission rather than the ESIPT keto-tautomer emission. This result also demonstrates that the EL emission comes from the emissive layer, and moreover, excimer or exciplex species are effectively suppressed. It is worth noting that the fullwidth at half-maximum (FWHM) of the EL spectrum is only about 53 nm, which is narrower than those of most previously reported deep-blue-emitting materials.^[2c,3,7] The OLED based on 3a exhibits a deep-blue electroluminescence with the CIE coordinates of (0.15, 0.08) very close to the NTSC coordinates of (0.14, 0.08) (Figure 4c). The EL spectra show little change under different current densities, indicating that the 3a-based device possesses excellent spectral stability (Figure 4b). Furthermore, the device exhibits a low turn-on voltage of 3.1 V and excellent performances with a maximum luminance of 9054 cd m⁻², CE of 5.04 cd A^{-1} , power efficiency (PE) of 4.89 lm W^{-1} , and EQE of 7.1% (Figure 4 and Table 3). In addition, under the luminance of 1000 cd m⁻², the device still has outstanding performances with CE of 3.43 cd A⁻¹ and EQE of 4.8%, which further demonstrates the robust stability of the device.

Given that the singlet exciton ratio is limited to a maximum of 25% due to the spin statistics, the EQE upper limit for classical fluorescent materials is about 5%.^[3] The device with **3a** as the emitter exhibits the highest EQE value of 7.1%, indicating a breakthrough in exciton utilization efficiency. Therefore, the radiative exciton yield (η_r) is calculated by Equation (1):^[3a]

$$\eta_{\rm r} = {\rm EQE}_{\rm max} / (\gamma \times \eta_{\rm PL} \times \eta_{\rm out}) = 7.1\% / (100\% \times 37.6\% \times 20\%) = 94\%$$
(1)

where EQE_{max} is the maximum external quantum efficiency; η_{out} is the light-out-coupling efficiency, which is about 20% in absence of out-coupling enhancement layer in the OLED; η_{PL} is the PL quantum efficiency of **3a** (13 wt% in CBZ₂-F₁), which was measured to be 37.6%; and γ is the recombination probability of injected holes and electrons in the emission layer, which is ideally 100%. Thus, the η_r value of the device with **3a** as the emitter was calculated to be 94%, which exceeds the upper limit of the singlet exciton ratio of 25% for conventional fluorescent OLEDs.

2.2.2. Electroluminescence Mechanism

To obtain further insight into the high exciton utilization efficiency exceeding 25% of the **3a**-based OLED, the EL

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Figure 4. a) Luminance–current density–voltage (*L*–*J*–*V*) characteristics of the **3a**-based device (13 wt% **3a** in CBZ_2 - F_1). b) The EL efficiency–current density and EQE–current density curve of the **3a**-based device. Inset: normalized EL spectra of the **3a**-based device operating at different current densities. c) CIE₁₉₃₁ coordinates of the device.

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triplet-triplet annihilation (TTA), thermally activated delayedfluorescence (TADF), and hybridized local and charge-transfer (HLCT) excited-state, as three main theoretical models that break through the singlet exciton statistics limit, have received considerable attention.^[7e,g,h,16,17,18] The TTA process can provide a theoretically maximized exciton utilization efficiency of 62.5% through triplet-triplet fusion to singlet excitons.^[7g,16] For 3a, the possibility of the TTA mechanism can be obviated, because its exciton utilization in OLED device is far more than 62.5%. TADF can realize a nearly 100% exciton utilization through thermally assisted reverse intersystem crossing (RISC) from the lowest triplet state (T_1) to the lowest singlet state (S_1) .^[7e,17] In order to reach thermal equilibrium of the relaxed excited states, TADF materials generally possess long fluorescence lifetime ($\tau_{\rm F} > 1 \,\mu s$) at room temperature.^[17c] The time-resolved PL measurement shows that the excited-state lifetime of 3a is only on the order of nanoseconds (ns) in both low- and highpolarity solvents (1.23 ns in hexane and 2.81 ns in acetonitrile) (Figure S4 and Table S4, Supporting Information). Moreover, the temperature-dependent transient PL measurement for 3a in the CBZ₂-F₁ film also shows no long-lifetime fluorescence component, as the temperature increases from 77 to 307 K (Figure S14 and Table S8, Supporting Information), indicating an essential difference between 3a and typical TADF materials in luminous mechanism.

The HLCT excited state is considered to be the coexistence or hybridization of locally excited (LE) and CT states. $^{\left[7h,18\right]}$ The LE state is beneficial to improving PL efficiency. The CT state offers the possibility for a small singlet-triplet energy level splitting (ΔE_{ST}), which can trigger a potential RISC (T \rightarrow S₁).^[18] Therefore, HLCT materials can provide high PL efficiency and exciton utilization of up to 100% through efficient RISC. As shown in Figures 1 and 2, the PL spectra of 3a present vibrational fine structure in low polar solvents including *n*-hexane, trimethylamine, toluene, n-butyl ether, and benzene, which reveals the existence of LE state. With the increase of solvent polarity, the fine structure of emission spectrum disappears, and 3a shows a gradually red-shifted solvatochromic behavior, demonstrating the CT feature in the excited state. In both low polarity and high polarity solvents, 3a exhibits only one slope of 10 956 (r = 0.98) in linear fitting of Lippert–Mataga model (Figure 2b and Section V, Supporting Information). The excitedstate dipole moment (μ_e) is calculated to be 16.3 D, which is slightly smaller than that of the typical CT molecule 4-(N,Ndimethylamino)-benzonitrile ($\mu_e = 23$ D), and larger than that of usual LE emitters (≈ 8 D).^[15,18] Moreover, **3a** also possesses a monoexponential decay of the excited state in various solvents (Figure S4 and Table S4, Supporting Information). These results indicate that the excited state of 3a consists of a sufficient or quasi-equivalent hybridization of LE and CT states.[7h,18d]

Furthermore, the natural transition orbitals (NTOs) of $S_1 \rightarrow S_0$ calculated by TD-M062X/6-31G(d, p) method also demonstrate that **3a** may possess the HLCT excited states in the EL process. As shown in Figure S15 (Supporting Information), the hole is mostly spread over the whole molecule skeleton, while the particle is mainly distributed on the conjugated backbone, except for the two phenyl rings resembling propeller blades. The hole and particle distributions are almost completely overlapped

Table 3. The device performances with 3a as the emitter.



Emitter	^{a)} (V)	CIE ₁₉₃₁ ^{b)} [<i>x</i> , <i>y</i>]	EQE _{max} c) [%]	CE _{max} ^{d)} [cd A ⁻¹]	PE _{max} ^{e)} [Im W ⁻¹]	L _{max} ^{f)} [cd m ⁻²]	Device pe	Device performances at 1000 cd m ⁻²		
							EQE [%]	CE [cd A ⁻¹]	PE [lm W ⁻¹]	
3a	3.1	(0.15, 0.08)	7.1	5.04	4.89	9054	4.8	3.43	1.89	

a) Turn-on voltage at a brightness of 1 cd m⁻²; ^b)0.1 mA cm⁻²; ^c) External quantum efficiency; ^d) Maximum current efficiency; ^e) Maximum power efficiency; ^f) Maximum luminance.

from the 2-(2-hydroxyphenyl)azole to the adjacent biphenyl, implying a LE featured transition of $S_1 \rightarrow S_0$. The hole-particle distributions are separated on the two outstretched phenyl rings of TPA, which demonstrates a CT featured transition. In addition, the energies of singlet and triplet excited states were also calculated (Table S9, Supporting Information). The energy levels of the lowest singlet state (S_1) is 3.567 eV, while the triplet state energies (T1, T2, and T3) are 2.778, 3.234, and 3.570 eV, respectively. The energy gap of S₁ and T₁ amounts to 0.789 eV, indicating that the TADF process by RISC from T₁ to S₁ is less likely to occur (Figure 5a and Table S9, Supporting Information).^[17] The energy levels of S_1 and T_3 are almost identical, implying a potential RISC process from T₃ to S₁. Moreover, the energy gap between T_3 and T_2 (0.336 eV) is much larger than that between T_3 and S_1 (0.003 eV), which demonstrates that the internal conversion rate from T_3 to T_2 may be lower than the RISC rate from T₃ to S₁.^[7h,18]

In the molecular structure of 3a, the oxazole and TPA moieties act as a weak acceptor (A) and a moderate donor (D), respectively, and the biphenyl unit between oxazole and TPA nitrogen-atom plays the role of π -bridge (Figure 5b). The slightly twisted biphenyl with the dihedral angle of 31.9° enables both the hole and the particle to partially delocalize to the whole molecule, rather than fully separate or localize, and therefore, is not only beneficial to the formation of the LE state, but also favors the generation of the CT state.^[18] In addition, the significantly twisted conformation between the biphenyl and the other two benzene rings of TPA with the dihedral angles of 66.65° and 60.88°, respectively, also may be responsible for the CT state. The intramolecular H-bond between phenol hydroxyl and oxazole plays an important role in maintaining the planarity of the 2-(2'-hydroxyphenyl)oxazole as well as suppressing the nonradiative rotational relaxation. It is worthy of note that the oxazole skeleton is seldom used as the acceptor in D-A type EL materials. This work presents the first example of highly efficient deep-blue EL materials employing the oxazole as an acceptor, which shows good CIE and high EQE over 5%.

3. Conclusions

In summary, the unusual luminescence properties of TPAbearing 2-(2'-hydroxyphenyl)oxazoles and their application in highly efficient deep-blue OLEDs have been investigated. The introduction of TPA into the side of oxazole of 2-(2'-hydroxyphenyl)oxazoles leads to a single enol-form emission and complete suppression of the ESIPT keto-form emission. Thus, the resulting compound only shows a deep-blue enol-form emission in both PL and EL spectra due to the absence of the keto-form emission at the long wavelength region. The doped device of **3a** with CBZ₂-F₁ host exhibits a high spectral stability and an excellent color purity with a narrow FWHM of 53 nm and the CIE coordinates of (0.15, 0.08), which are very close to the CIE (0.14, 0.08) of the NTSC standard blue. The maximum luminance, CE, PE, and EQE of device are 9054 cd m⁻², 5.04 cd A⁻¹, 4.89 lm W⁻¹, and 7.1%, respectively. The exciton utilization of the device is calculated to be 94%, which exceeds the theoretical limit of the singlet exciton ratio of 25% for conventional fluorescent OLEDs. Experimental data and theoretical calculations demonstrate that 3a possesses a HLCT excited state character, which consists of a sufficient or quasi-equivalent hybridization of LE and CT states. The slightly twisted π -conjugated backbone of **3a** is beneficial to both the formation of LE state and the generation of CT state. The intramolecular H-bond between phenol hydroxyl and oxazole plays an important role in maintaining the molecular planarity and suppressing the nonradiative rotational relaxation. As a result, 3a features a high PL efficiency and exhibits a high exciton utilization efficiency of nearly 100% with EQE up to 7.1% in OLEDs.



Figure 5. a) The simple model for exciton relaxation in the EL process and calculated singlet-triplet energy of 3a. b) Molecular conformation of 3a.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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