

Perturbing Localization of Electron Distribution in Thermally Activated Delayed Fluorescence Emitters for Efficient Red Electroluminescence

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Abstract. To compete with the severe non-radiative decay in long-wavelength emission, fast radiative decay is significantly required. Due to good rigidity and strong electron-donating ability, phenoxazine (PXZ) is a promising donor group to be applied in long-wavelength thermally activated delayed fluorescence emitters. However, PXZ-based molecules show highly twisted geometry, which reduces the oscillator strength and limits their performance. Herein, we demonstrate that the oscillator strength can be enhanced without compromising the molecular rigidity by strategically increasing localization of electron distribution in PXZ-based emitters. The corresponding red organic light-emitting diode showed a maximum external quantum efficiency of 11.7%, demonstrating an improvement of 39% compared with the control group.

Keywords: Electron distribution, efficient red electroluminescence, phenoxazine (PXZ).

1. Introduction

Thermally activated delayed fluorescence (TADF) emitters have been emerging as a new class of materials that demonstrate great potential for high-efficiency organic light-emitting diodes (OLEDs). [1–5] Benefiting from the small singlet-triplet energy gap (ΔE_{ST}), full exciton utilization can be achieved by reverse intersystem crossing of triplet excitons. Among the three primary color emitters, red emitters have developed more slowly and face greater limitations in molecular design. This is because the non-radiative decay exponentially increases as the emission shifts towards the red region. [6] Strengthening the molecular rigidity to reduce the structural relaxation is an effective approach to mitigate the energy loss. [7] However, according to our previous summary and analysis, the fast radiative decay resulting from strong conjugation proves more advantageous than increasing rigidity, [8] which explains why triphenylamine has become the most widely used electron-donating group in long-wavelength emitters. Phenoxazine (PXZ), a planar and bulky unit with good rigidity and a shallower highest occupied molecular orbital (HOMO) energy level than triphenylamine, is another promising candidate to construct efficient red TADF emitters. However, common molecular design strategies, such as introducing intramolecular hydrogen bonding to enhance conjugation, may not be applicable to PXZ-based emitters. Because this would lead to different conformational distribution in the aggregation state, which significantly impacts their properties. [9] Therefore, a strategy that increases the oscillator strength without compromising the molecular rigidity is essential for optimizing PXZ-based emitters.

In this work, a strategy was proposed that improves the electron-hole coupling by strategically perturbing the electron distribution. 10-(dipyrido[3, 2-a:2', 3'-c]phenazin-11-yl)-10H-phenoxazine (PXZ-2NP) was designed by attaching PXZ to an N-heterocyclic polycyclic aromatic acceptor group. [10] The strong conjugation induces a small energy gap for red emission and the fused-ring structure ensures good rigidity. For further optimization, the nitrogen location of the acceptor was modulated. 10-(dibenzo[f, h]pyrido[2, 3-b] quinoxalin-12-yl)-10H-phenoxazine (PXZ-QP) was designed by concentrating the nitrogen atoms, which perturbed the localization of electron distribution and consequently enhanced the oscillator strength. As the nitrogen atom is positioned at the remote end of PXZ, the conformational distribution is minimally affected. A larger electron/hole overlap was

observed at the 10-position nitrogen in PXZ-QP, contributing to a greater oscillator strength of 0.044. Both two emitters show photoluminescence (PL) peaks around 600 nm. As for electroluminescence (EL), the PXZ-QP-based device demonstrated maximum external quantum efficiency (EQE_{max}) of 11.7% with an emission peak of 600 nm, 39% higher than that based on PXZ-QP. This work provides a feasible approach to precisely enhance the conjugation for highly twisted emitters by perturbing the electron distribution.

2. Experimental Section

2.1 General

The ^1H and ^{13}C NMR spectra were recorded via an Agilent DD2 400-MR spectrometer at room temperature. The UV-visible absorption spectra were measured with a Shimadzu UV-2600 spectrophotometer and the photoluminescence spectra were recorded on a Hitachi F-4600 fluorescence spectrometer. Transient photoluminescence decay spectra were obtained with Horiba Single Photon Counting Controller: FluoroHub and Horiba TBX Picosecond Photon Detection. Indium tin oxide (ITO) glass substrates with a sheet resistance of $15\ \Omega$ per square were firstly cleaned with acetone, ethanol, and deionized water, and then dried in an oven at $120\ ^\circ\text{C}$ for 2 h. Prior to being put into the thermal deposition instrument, the substrates were treated with UV-ozone for 20 minutes. All devices were fabricated by evaporating organic layers at a rate of $0.1\text{--}0.15\ \text{nm s}^{-1}$ onto the ITO substrate sequentially at a pressure below 5×10^{-4} Pa. LiF was deposited at a rate of $0.1\ \text{nm s}^{-1}$ for electron injection. Al was deposited at a rate of $1\ \text{nm s}^{-1}$ as the cathode. The optical and electrical data of the devices were obtained with a PR655 Spectrscan and Keithley 2400 Source Meter under ambient atmosphere simultaneously.

2.2 Synthesis

Synthesis of 10-(dipyrido[3, 2-a:2',3'-c] phenazin-11-yl)-10H-phenoxazine (PXZ-2NP)

11-bromodipyrido[3, 2-a:2', 3'-c] phenazine (intermediate 1) was prepared according to our previous report. [10] A mixture of intermediate 1 (722.4 mg, 2.0 mmol), 10H-phenoxazine (403.1 mg, 2.2 mmol), $\text{Pd}(\text{OAc})_2$ (22.5 mg, 0.1 mmol), $(t\text{-Bu})_3\text{P}$ (40.5 mg, 0.2 mmol), and $t\text{-BuONa}$ (384.4 mg, 4.0 mmol) was added into a round bottom flask (100 mL) under nitrogen. 25 mL toluene was added to the reaction afterwards, and the mixture was refluxed for 24 h. TLC was used to detect the completion of reaction. After cooling to room temperature, the solvent was evaporated under vacuum. The residue solid was purified by column chromatography and recrystallization to give the product as brown solid (565.5 mg, yield 61%). ^1H NMR (600 MHz, Methylene Chloride- d_2) δ 9.67 – 9.53 (m, 2H), 9.22 (ddt, $J = 16.7, 4.0, 1.8\ \text{Hz}$, 2H), 8.54 (dd, $J = 8.9, 1.5\ \text{Hz}$, 1H), 8.47 (t, $J = 1.8\ \text{Hz}$, 1H), 7.91 – 7.69 (m, 3H), 6.77 – 6.49 (m, 6H), 6.10 (d, $J = 8.1\ \text{Hz}$, 2H). ^{13}C NMR (151 MHz, Methylene Chloride- d_2) δ 152.73, 152.69, 144.13, 133.75, 133.70, 133.69, 133.07, 132.92, 131.79, 124.34, 123.42, 122.17, 115.75, 113.68, 53.95, 53.77, 53.59, 53.41, 53.23. MALDI-TOF-MS: calculated $[\text{M}-2\text{H}]^-$ for $\text{C}_{30}\text{H}_{17}\text{N}_5\text{O}^- = 461.1265$, found 461.4533.

Synthesis of 10-(dibenzo[f, h] pyrido[2, 3-b] quinoxalin-12-yl)-10H-phenoxazine (PXZ-QP)

The synthetic procedures were the same as PXZ-2NP, only to replace intermediate 1 with 12-bromodibenzo [f, h] pyrido [2, 3-b] quinoxaline (intermediate 2). Red solid 590 mg, yield 69%. ^1H NMR (600 MHz, Methylene Chloride- d_2) δ 9.31 (dd, $J = 28.8, 8.0\ \text{Hz}$, 2H), 8.50 (dd, $J = 44.3, 8.5\ \text{Hz}$, 3H), 8.35 – 8.26 (m, 1H), 7.83 – 7.63 (m, 4H), 6.75 – 6.46 (m, 6H), 6.06 (d, $J = 8.0\ \text{Hz}$, 2H). ^{13}C NMR (151 MHz, Methylene Chloride- d_2) δ 126.35, 123.48, 123.21, 121.98, 115.68, 113.79, 53.94, 53.76, 53.58, 53.40, 53.22. MALDI-TOF-MS: calculated $[\text{M}-3\text{H}]^-$ for $\text{C}_{31}\text{H}_{18}\text{N}_4\text{O}^- = 459.1229$, found 459.5202

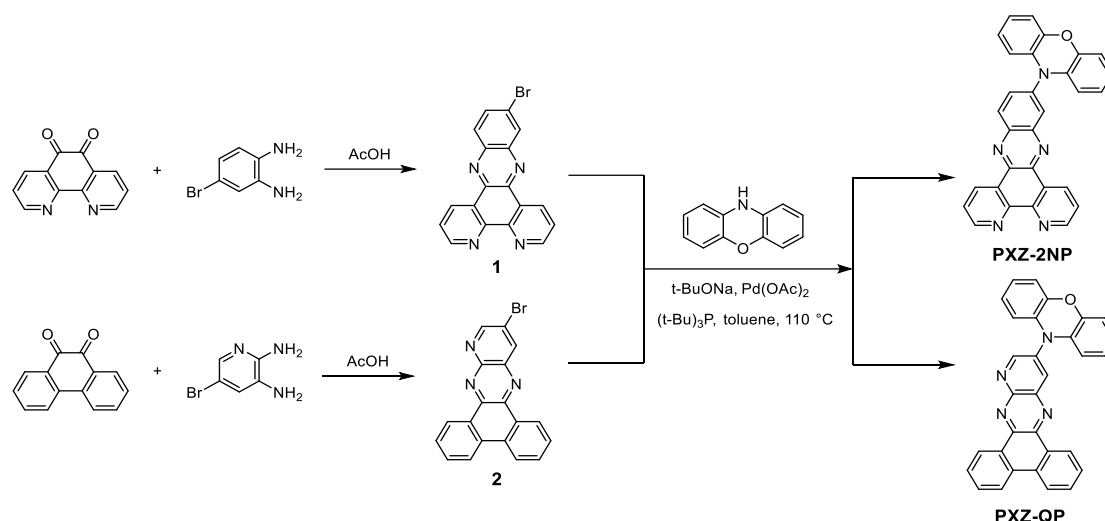


Figure 1. Scheme 1. Synthetic routes of PXZ-2NP and PXZ-QP

3. Results and Discussion

As shown in Fig 1: Scheme 1, both PXZ-2NP and PXZ-QP were readily synthesized by dehydration cyclization and C-N cross-coupling using commercial reagents to give good yield. Density functional theory (DFT) was used to study their ground-state properties. The geometries were optimized at the B3LYP/6-31G(d) level using Gaussian 16. As shown in Figure 2, the donor-acceptor dihedral angle of PXZ-QP (74.1°) is slightly smaller than that of PXZ-2NP (75.7°). The HOMO is distributed on PXZ and the lowest unoccupied molecular orbital (LUMO) is distributed on the nitrogen-fused acceptor plane. The spatially separated frontier molecular orbitals lead to small overlap, which is beneficial for a small ΔE_{ST} . The HOMO energy levels of PXZ-2NP and PXZ-QP are calculated to be -4.83 and -4.84 eV, respectively. The LUMO energy levels are respectively -2.66 and -2.64 eV for PXZ-2NP and PXZ-QP. Furthermore, their first excited singlet states (S_1) were studied using time-dependent DFT (TD-DFT), calculated using the optimized ground state structure. The electron-hole analysis was carried out using Multiwfn.[11,12] The electron distribution is perturbed when replacing the carbon atom at 10-position with nitrogen. As a result, the oscillator strength of PXZ-QP is enhanced from 0.039 to 0.044. The slight localization of electron distribution is achieved simultaneously ensuring the overall molecular rigidity, preventing the variation of conformational distribution. To gain more insights, the overlap between electron and hole distribution is demonstrated. The two emitters have similar isosurface distribution except that the 10-position nitrogen of PXZ-QP has a larger overlap than the 10-position carbon of PXZ-2NP, further confirming that the enhancement of oscillator strength originated from the acceptor optimization. The Sr index, which describes the extent of hole/electron overlap, was also calculated using Multiwfn. A larger value of 0.27 was obtained for PXZ-QP.

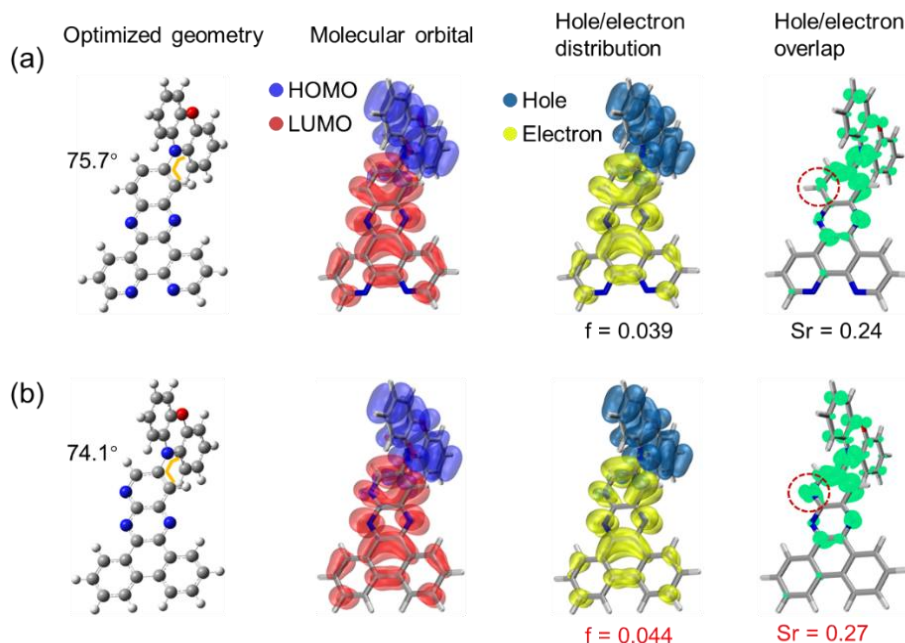


Figure 2. Ground state optimized geometries, HOMO/LUMO distribution, hole/electron distribution and the overlap of S_1 state of PXZ-2NP (a) and PXZ-QP (b), f represents oscillator strength

UV-vis absorption spectra of PXZ-2NP and PXZ-QP were recorded as shown in Figure 3a. The absorption between 300 and 400 nm is attributed to π - π^* and n - π^* transitions of the donors and acceptors, while the structureless bands from 410 to 510 nm are the results of intramolecular charge transfer. A widely used host 4,40-di(9H-carbazol-9-yl)-1,10-biphenyl (CBP) was selected to disperse the emitters for its suitable energy levels. Under 1 wt% doping concentration, red emission peaked at 593 and 604 nm was observed for PXZ-QP and PXZ-2NP, respectively (Figure 3b). In addition, transient PL spectra were also recorded to verify their TADF characteristic. As shown in Figure 3c, the decay curves of both emitters show biexponential characteristic. The nanosecond-scale prompt components of PXZ-QP and PXZ-2NP are fitted to be 19.0 and 19.7 ns, and their delayed lifetimes are 65.7 μ s and 32.8 μ s, respectively. The notably longer lifetime of PXZ-QP may be ascribed to larger ΔE_{ST} induced by the strong conjugation.

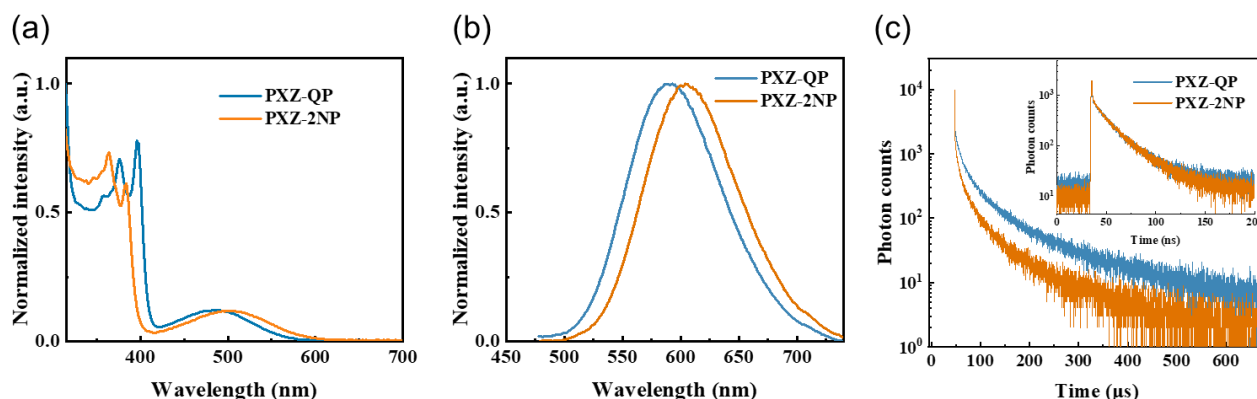


Figure 3. Normalized absorption spectra in dilute toluene (10^{-5} M) (a), normalized solid-state (CBP:1 wt% emitter) PL spectra (b) and solid-state transient PL decay curves (c) of PXZ-2NP and PXZ-QP

Multilayer OLEDs with a structure of ITO/4, 4'-(cyclohexane-1, 1-diyl) bis (N, N-di-p-tolylaniline) (TPAC, 35 nm)/Tris(4-(9H-carbazol-9-yl) phenyl) amine (TCTA, 10 nm)/CBP:1 wt% emitters (20 nm)/3, 3'-(5'-(3-(pyridin-3-yl) phenyl)-[1, 1':3', 1''-terphenyl]-3, 3''-diyl) dipyrindine (TmPyPB, 50 nm)/LiF (1 nm)/Al (100 nm) were fabricated to study the EL properties. Consistent with their PL

emission, PXZ-QP- and PXZ-2NP-based devices show red emission with peaks at 600 and 608 nm (Figure 4a). The turn-on voltage of the devices is about 3.8 V. PXZ-QP-based OLED have higher maximum luminance of 12600 cd m^{-2} . More importantly, the device using PXZ-QP as the emitter demonstrates higher maximum current efficiency, power efficiency and EQE of 25.1 cd A^{-1} , 20.7 lm W^{-1} and 11.7%. These values are superior to those of the device using PXZ-2NP, which exhibits 14.6 cd A^{-1} , 10.8 lm W^{-1} , and 8.39%. The more concentrated nitrogen atom distribution in PXZ-QP enhances the oscillator strength, favorable for a fast radiative decay, thus improving the device performances.

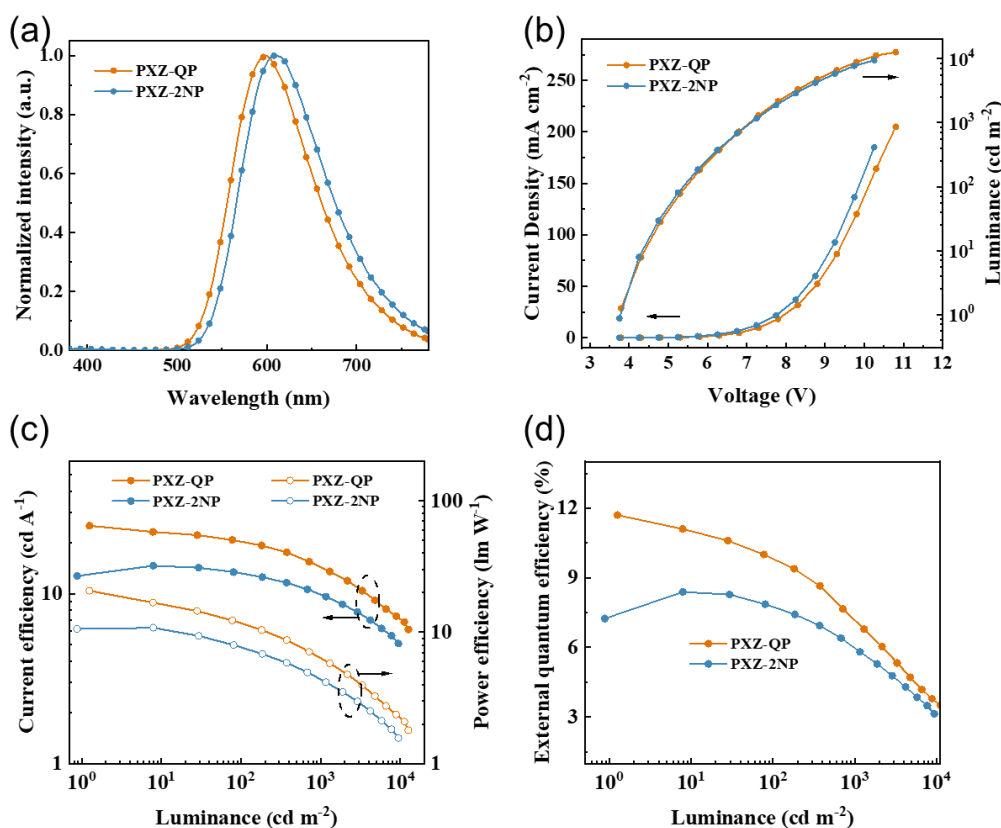


Figure 4. (a) EL spectra at 100 cd m^{-2} , (c) Current density-voltage-luminance curves and (d) EQE-luminance plots of TPA-DCPPy-, TPA-DCPPm- and TTPA-DCPPm-based OLEDs

4. Conclusion

In summary, two red TADF emitters with similar emission but different electron distribution were designed and synthesized. By concentrating the nitrogen atoms, a slight modulation of electron distribution is achieved, enhancing the oscillator strength of PXZ-QP without compromising the molecular rigidity. Consequently, PXZ-QP-based OLED exhibit a 39% improvement in EQE_{max} and similar emission compared with PXZ-2NP-based device. This work offers insights to modulate the conjugation strength of highly twisted structures and may propel the development of long-wavelength TADF emitters.

Acknowledgments

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