



Fine-tuning the emissions of highly efficient thermally activated delayed fluorescence emitters with different linking positions of electron-deficient substituent groups



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ABSTRACT

To further develop a simple method for emission fine-tuning, two novel thermally activated delayed fluorescence (TADF) emitters, 5'-(10H-phenoxazin-10-yl)-[1,1':3',1''-terphenyl]-2',4,4''-tricarbonitrile (mPTBC) and 2'-(10H-phenoxazin-10-yl)-[1,1':3',1''-terphenyl]-4,4'',5'-tricarbonitrile (oPTBC) have been designed and synthesized by employing exactly the same functional units, a ter-benzonitrile and a phenoxazine (PXZ). By adjusting the linking position of the two electron-deficient benzonitrile arms from a *meta*-position to an *ortho*-position with the cyano core, the LUMO energy levels of mPTBC and oPTBC are varied to -2.98 and -3.13 eV, respectively; while the HOMO energy levels remain similar. In devices, the new TADF emitters successfully exhibit similar maximum efficiencies, but different-color emissions with a spectral peak at 516 nm for mPTBC and a spectral peak at 540 nm for oPTBC. These results prove the simple modification of adjusting the linking position of electron-deficient substituent groups in the molecules can effectively fine-tune the emissions of TADF emitters but without significantly changing other key performance.

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1. Introduction

Organic light-emitting devices (OLEDs), on account of their potential applications in large-area displays and solid state lighting, have attracted great interest in the past few decades [1–5]. Based on the quantum statistics, electro-excitation produces singlet and triplet excitons with a ratio of 1:3 [6]. Conventional fluorescent emitters can only utilize singlet excitons and limit their theoretical internal quantum efficiency (IQE) of only 25% in the devices. By introducing noble metal (such as Pt and Ir) complexes as the

emitters, phosphorescent OLEDs can theoretically reach 100% IQE [7], however, accompanied with high cost and heavy metal pollution. To address this feature OLEDs based on thermally activated delayed fluorescence (TADF) emitters came as a bright alternative option and have been widely studied in recent years [8–12], for they can also realize 100% IQE without assistance of noble metals.

Due to the extremely small singlet-triplet energy gaps (ΔE_{ST}), TADF emitters can possess efficient reverse intersystem crossing (RISC) process from the triplet (T1) to the singlet (S1) excited states, thus potentially realize full exciton utilization in the devices. Currently, the most common way to build TADF emitters is combining electron-donor (D) and electron-acceptor (A) segments in a twisted arrangement (with a large dihedral angle) [13,14], aiming to minimize the overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the molecules [15]. Various heterocycles, such as phenoxazine (PXZ), dimethylacridine and carbazole group for D segments and cyano, sulfone and carbonyl group for A segments

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[9,10,16–19], have been applied to develop efficient TADF emitters with different emission profiles. However, due to the limitation of selectable organic groups, the emissions of TADF emitters can't be optionally adjusted just by the selection of D and A segments. Thus, it is always a great challenge to develop a simple method for fine regulation on the emissions of the TADF emitters [20]. In 2013, Adachi et al. [21], reported emission tuning of three TADF emitters with the same D and A segments except the number of D units. In 2016, Yasuda et al. [22], reported a series of phthalonitrile and dicyanopyrazine based derivatives, and realized various color emission via the modification on A segments of the TADF emitters. Pan et al. [23], reported a series of CN-substituted N-containing heterocyclic based TADF emitters, and studied the influence on the emission of different acceptor strengths and tunable conformations. Recently, our group has also studied the relationship between structural rigidity and color purity for TADF emitters [24].

To further develop a simple method for emission fine-tuning, in this work, we designed and synthesized two isomeric TADF emitters 5'-(10H-phenoxazin-10-yl)-[1,1':3',1''-terphenyl]-2',4,4''-tricarbonitrile (mPTBC) and 2'-(10H-phenoxazin-10-yl)-[1,1':3',1''-terphenyl]-4,4'',5'-tricarbonitrile (oPTBC) as shown in Scheme 1. Both emitters employ ter-benzonitrile as the A segment and PXZ as the D segment to form a common D-A skeleton [11,16,25], and successfully realize extremely small ΔE_{ST} of 0.006 and 0.007 eV for mPTBC and oPTBC, respectively, insuring the TADF characteristics. By adjusting the linking position of two electron-deficient benzonitrile arms from meta-position to ortho-position with the cyano core, the LUMO energy levels of mPTBC and oPTBC are obviously varied to -2.98 and -3.13 eV, respectively. While the HOMO energy levels of two TADF emitters remain at the close values (-5.37 and -5.38 eV) due to the nearly complete separations between their HOMO and LUMO [26]. Accordingly, two TADF emitters successfully exhibit different energy gaps and different-color emissions. In the OLEDs, the device based on mPTBC shows green emission with a CIE coordinate of (0.29, 0.56), a peak at 516 nm and a high maximum EQE of 18.1%, whereas oPTBC-based device exhibits yellow-green emission with a CIE coordinate of (0.35, 0.56), a

peak at 540 nm and a high maximum EQE of 17.8%. These results further confirm that the emissions of the TADF emitters can be fine-tuned by the simple modification of adjusting the linking position of electron-deficient substituent groups.

2. Experimental

2.1. General methods

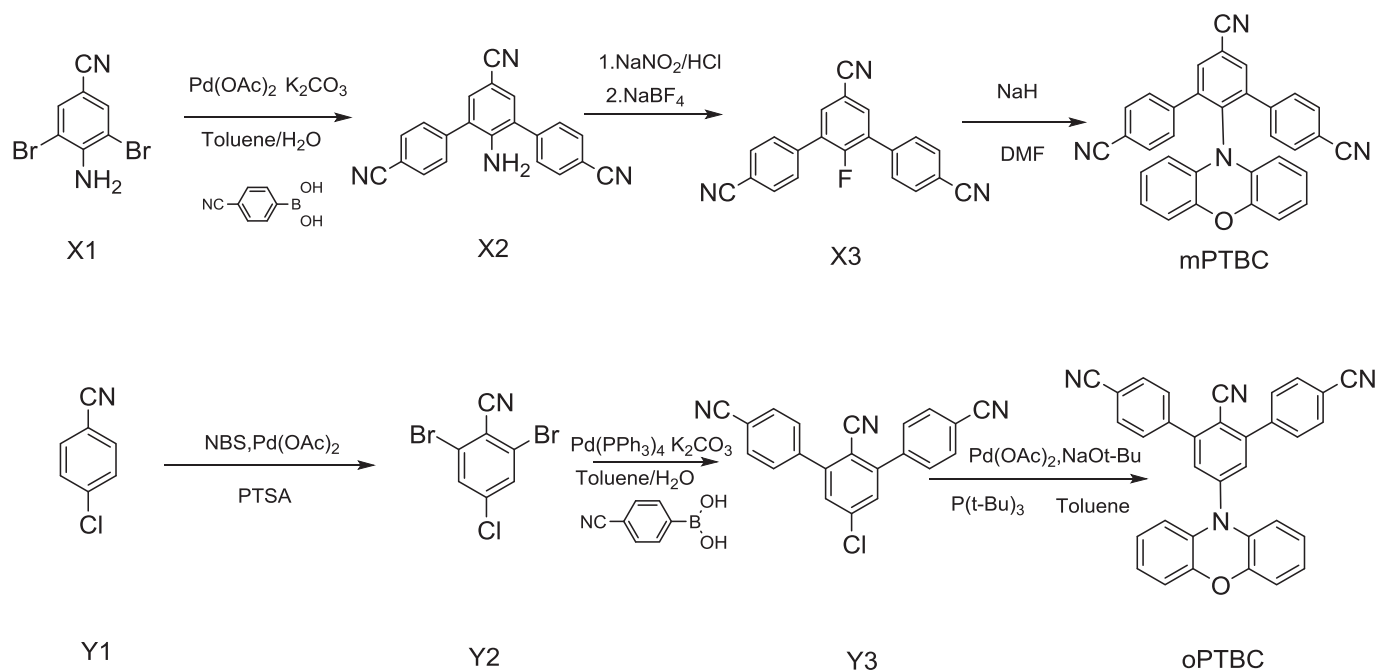
All of the starting materials and solvents used for synthesis were purchased from J&K Corp., (China) and used without further purification. The ^1H NMR and ^{13}C NMR spectra were recorded using an AVANCZ spectrometer at 298 K in DMSO- d_6 and CDCl_3 solvents. MS data was measured via Finnigan 4021C gas chromatography mass spectrometry instrument. UV–vis and PL spectra were obtained via Hitachi UV–vis spectrophotometer U-3010 and Hitachi fluorescence spectrometer F-4600, respectively. Edinburgh Instruments FLS920 spectrometer gave the transient PL. Cyclic voltammetry measurements were measured on a CHI660E electrochemical analyzer. The photoluminescence quantum yield of doped mCP solid film was investigated via QY-2000 fluorescence spectrometer and estimated via an F-3018 integrating sphere under ambient atmosphere. Moreover, DSC and TGA measurements were also measured in a N_2 atmosphere.

2.2. Synthesis

The synthesis process of mPTBC and oPTBC was shown in Scheme 1.

2.2.1. Synthesis of 2'-amino-[1,1':3',1''-terphenyl]-4,4'',5'-tricarbonitrile (X2)

A mixture of 4-amino-3,5-dibromobenzonitrile (X1) (2.76 g, 10 mmol), 4-Cyanophenylboronic acid (3.23 g, 22 mmol), Tetraakis(triphenylphosphine)-palladium (0.56 g, 0.5 mmol, 5 mol%) and potassium carbonate (8.34 g, 60 mmol) were added into a clean 200 mL flask. The mixed solvent (toluene: 60 mL, H_2O : 25 mL,



Scheme 1. Synthetic routes and molecule structures of mPTBC and oPTBC.

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