



Non-doped blue organic light emitting devices based on tetraphenylethylene- π -imidazole derivatives



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ABSTRACT

Three tetraphenylethylene (TPE) conjugates **3a–3c** were designed and synthesized for non-doped blue organic light emitting diodes, where aryl imidazoles of phenanthrene, phenanthroline, and pyrene were coupled with TPE. The single crystal structures of **3a** and **3c** show twisted molecular geometry and the crystal packing of **3c** exhibits tight packing compared to **3a**. The thermal, photophysical, electrochemical and computational properties of **3a–3c** were investigated. The TPE conjugates **3a–3c** show good thermal stability upto 424 °C. All the TPE conjugates **3a–3c** exhibit excellent aggregation induced emission (AIE) and fluorescence of **3a**, **3b** and **3c** in aggregated suspension was enhanced by 9, 9 and 38 folds compared to fluorescence in THF solution, respectively. **3a** and **3c** were efficient as the non-doped fluorescent emitters and provided high quantum efficiency/current efficiency of 5.6%/11.1 cd/A and 5.0%/9.4 cd/A in the blue devices, respectively. The color coordinates of the **3a** and **3c** devices were (0.19, 0.31) and (0.18, 0.26), respectively.

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1. Introduction

Blue organic light emitting diodes (OLEDs) have gained considerable attention of the scientific community due to their importance in full-color display and solid-state lighting [1]. Myriads of attempts have been made for the development of efficient blue OLEDs [2]. The conventional fluorescent molecules suffer from the aggregation caused quenching (ACQ) due to π - π stacking interactions in the planar fluorophores, which limits their applicability in the efficient OLEDs [3]. Tang et al. introduced concept of aggregation induced emission (AIE) in 2001 and proved that AIE can effectively overcome the drawbacks of ACQ [4]. The AIE active molecules have very less chances of π - π stacking interactions due to their non-planar architecture, and work on the principle of restricted intramolecular rotation (RIR), and exhibit strong emission in the aggregated state.

The phenanthrene, phenanthroline and pyrene are widely

studied fluorophores for developing blue OLEDs due to their excellent thermal stability, long fluorescence lifetime, high charge carrier mobility and blue colored fluorescence with high quantum yield [5]. Lee et al. and Yang et al. have shown phenanthroimidazole- π -triphenylamine derivatives can be efficiently used for development of non-doped blue OLEDs [6]. The synthesis of solid state fluorescent material is one of the good methods to increase the efficiency of the devices.

The tetraphenylethylene (TPE) has been widely explored for AIE phenomenon and used to develop OLED materials [7]. Tang et al. have reported triphenylethene substituted phenanthroimidazole as the non-doped AIE type emitter for the design of efficient deep blue OLEDs [8]. However, the quantum efficiency (QE) of the non-doped blue OLEDs was below 5.0%. Therefore, we are interested in the synthesis of high efficiency non-doped blue light emitters in the solid state by using the TPE as the AIE active unit. Herein, we have synthesized three TPE conjugates **3a–3c** (Chart 1), where aryl imidazoles of phenanthrene, phenanthroline, and pyrene were coupled with TPE. The AIE properties of the TPE conjugates were discussed and the OLED properties of the non-doped **3a–3c** device were investigated.

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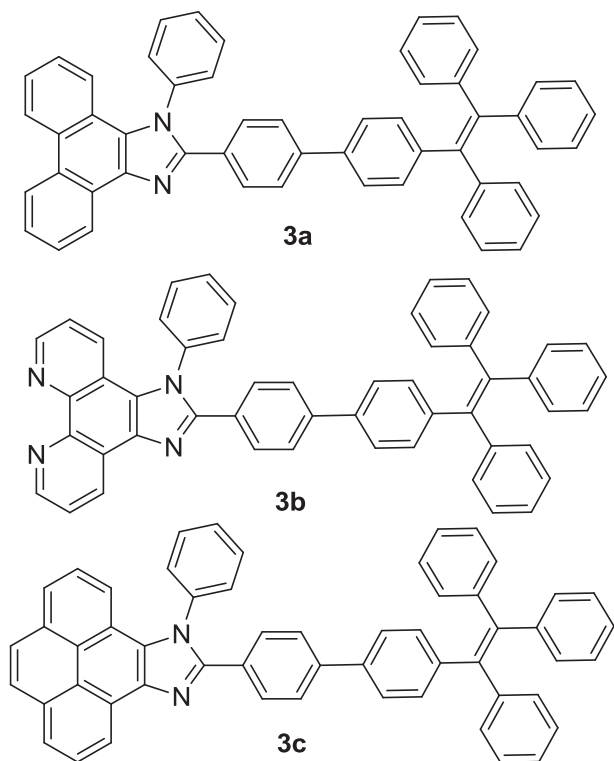


Chart 1. Molecular structures of TPE conjugates **3a–3c**.

2. Results and discussions

2.1. Synthesis

The TPE conjugates **3a–3c** were synthesized by the Suzuki cross-coupling reaction of TPE boronate ester with corresponding bromo-imidazoles **2a–2c** in 67%, 55% and 93% yields, respectively (Scheme S1) [9]. The bromo-imidazoles **2a–2c** were synthesized by the condensation reaction of diketone quinones **1a–1c** (phenanthrene-9, 10-dione **1a**, 1, 10-phenanthroline-5, 6-dione **1b** and pyrene-4, 5-dione **1c**) with aniline and 4-bromobenzaldehyde in 74%, 69%, and 76% yields, respectively. The intermediates **2a–2c** were purified by crystallization in methanol, whereas **3a–3c** were purified by column chromatography followed by crystallization from dichloromethane:hexane or dichloromethane:ethanol mixture. All the intermediates and products were characterized by ^1H NMR, ^{13}C NMR, and high resolution mass spectrometry (HRMS) techniques. The **3a** and **3c** were also characterized by single crystal X-ray analysis and the crystal structures are given in the supporting information. The crystal structure of **3a** and **3c** exhibits twisted conformation of phenyl rings and planar aryl imidazole unit (Fig. S1). This twisted conformation supports active intramolecular rotation in solution leading to poor fluorescence. The packing diagrams of both **3a** and **3c** exhibit almost similar packing framework. In the packing diagram of **3a**, the two mutual C–H– π (2.938 Å) and C–H– π (2.799 Å) interactions were observed (Fig. S2) whereas in the packing diagram of **3c**, three mutual C–H– π (3.070 Å), C–H– π (2.765 Å) and C–H– π (3.011 Å) interactions exist (Fig. S3). Thus, packing diagram of **3c** reveals tight packing compared to **3a** with one extra C–H– π interaction.

The thermal stability of TPE conjugates **3a–3c** was analyzed by the thermogravimetric analysis (TGA) (Fig. S4), and the data are listed in Table 1. The high thermal stability was found for **3a–3c**, the

thermal decomposition (T_d) temperatures corresponding to 5% weight loss under a nitrogen atmosphere were found to be 334 °C, 424 °C, and 404 °C for **3a**, **3b** and **3c**, respectively. The rigid aryl imidazole moieties of phenanthrene, phenanthroline, and pyrene were responsible for the high thermal stability of the three compounds.

2.2. Photophysical properties

The electronic absorption, and fluorescence spectra of TPE conjugates **3a–3c** were recorded in dichloromethane solution (Fig. S5) and corresponding data are listed in Table 1. The **3a–3c** show broad absorption bands in 250–400 nm region. The absorption spectra show multiple absorption peaks corresponding to the absorption of their aryl imidazole core. The electronic transitions in **3a–3c** can be assigned as π – π^* transitions. The red shift in the absorption maxima at longer wavelength region follows the order **3c** > **3a** > **3b**. The **3a–3c** are poorly fluorescent in solution due to loss of excited state energy by intramolecular rotations of TPE unit. The **3a**, **3b** and **3c** emit at 409, 432, and 427 nm with 0.009, 0.004, and 0.003 quantum yields in solutions, respectively.

The small aggregates of **3a–3c** were prepared and their AIE nature was studied by using fluorescence spectroscopy. The TPE conjugates are highly soluble in tetrahydrofuran (THF), and sparingly soluble in water. The nano aggregates of **3a–3c** were prepared by gradual increase in percentage of water in THF (Fig. 1 and Fig. S6). The free molecular rotations of TPE unit in aggregates were ceased and resulted in enhanced fluorescence intensity. The AIE study of **3a–3c** reveals the emission intensity starts increasing prominently by more than 80% of water fraction (f_w) in THF, and new peak was observed at 482 nm, 483 nm and 471 nm respectively. The fluorescence of **3a–3c** in aggregated suspension (95% aqueous mixture) was enhanced by 9, 9 and 38 folds (Fig. 1), compared to fluorescence in THF solution respectively.

2.3. Electrochemical properties

The electrochemical properties of **3a–3c** were explored by the cyclic voltammetric analysis in dichloromethane (DCM) solution using tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. The cyclic voltammogram is presented in Fig. S7, and the data are listed in Table 1. The potentials were measured vs Ag/Ag⁺ as quasi reference electrode. The HOMO energy level was estimated from the onset oxidation potentials of the first oxidation peak. The HOMO energy level was calculated using expression,

$$E_{HOMO} = -[E_{ox}^{onset} + 4.4]$$

The highest occupied molecular orbital (HOMO) values for **3a**, **3b**, and **3c** were estimated from onset oxidation potential and are –5.41, –5.63 and –5.34 eV, respectively. Their LUMO values were obtained by addition of the HOMO value to band gap (E_g) estimated from the onset absorption. The calculated LUMOs are –2.42, –2.63 and –2.42 eV for **3a**, **3b**, and **3c**, respectively. The HOMO and LUMO energy levels of **3b** were stabilized due to the electron deficient nature and heteroaromatic character of the phenanthroline.

2.4. Theoretical study

In order to understand the electronic and photophysical properties of **3a–3c**, theoretical calculation was performed. The density functional theory (DFT) calculations were carried out at the B3LYP/6–31G (d) level in the Gaussian 09 program [10]. The energy minimized structures for **3a–3c**, show non planar structure of TPE

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