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Non-doped OLEDs based on tetraphenylethylene phenanthroimidazoles with negligible efficiency roll-off: Effect of end groups regulated stimuli responsive AIE luminogens

Jayaraman Jayabharathi*, Shanmugam Thilagavathy, Venugopal Thanikachalam

Department of Chemistry, Annamalai University, Annamalai nagar, Tamilnadu- 608 002, India

Abstract

The positional isomers of phenanthroimidazoles, TPE-NPPB and TPE-APPB have been designed to understand the positional effect of triphenylamine (TPA) and tetraphenylethylene (TPE) units on aggregation induced emission and mechanochromism. Phenanthroimidazoles, TPE-NPPB and TPE-APPB show reversible mechanochromism between blue and green colours and was analysed by powder X-ray diffraction (PXRD). PXRD analysis reveal that phase transition of TPE-NPPB and TPE-APPB from crystalline to amorphous state may attributed with colour changes. The non-doped OLEDs based on TPE-NPPB and TPE-APPB exhibit high external quantum efficiency (EQE) of 3.2 and 5.3%, current efficiency (CE) of 4.32 and 5.28 cd/A and power efficiency (PE) of 4.01 and 4.92 lm/W, respectively. The improvement of mechanochromic materials with aggregation induced emission (AIE) behaviour play vital role in optoelectronics.

Key Words: Positional effect, Triphenylamine (TPA), Tetraphenylethylene (TPE), High efficiency, Mechanochromism, AIE.
Introduction

Luminescent materials are commonly used in organic light-emitting diodes (OLEDs) and used as chemosensor as well as mechano-sensors [1-3]. Organic materials with tunable solid state emission is in progress due to their utility in memory devices, security systems, data storage, etc., [1, 2]. Mechanochromic materials altered their colours on applying external mechanical stimuli such as grinding, rubbing and crushing [1, 3]. A prerequisite for reversible mechanochromism is high solid state emission which depends on planarity, effective conjugation and interaction with surrounding environment [4-6]. However, conventional organic materials suffer from aggregation caused quenching (ACQ) which decreases the luminance efficiency [7-9]. Aggregation induced emission (AIE) is a promising solution to ACQ [10-13], Mechanochromic materials with AIE behaviour become highly emissive in solid state and can be employed as emissive materials in OLEDs [14].

The luminescence properties of materials in solid state depends on molecular arrangement as well as intermolecular interactions [14]. The mode of molecular packing of the materials will affect molecular stacking as well as conjugation and tuned the luminescence properties [15]. Thus, monitoring molecular packing is significant in altering the photophysical and electroluminescent properties [15–17]. Phenanthroimidazole exhibits near-ultraviolet emission with electron-transport ability. Its twisted and rigid molecular structure can enhance the stability and carrier transport ability [18-20]. To shift the emission maximum to visible region, electron-donating triphenylamine (TPA) group was incorporated into the molecule. Organic emitters containing TPA group used as hole transport materials because of their unique optoelectronic properties which include the electron-donating ability and high hole mobility. Although TPA can be used as a complexing agent in high temperature superconducting materials, it causes ACQ effect in solids. Therefore, introducing an aggregation-induced emission (AIE) group such as triphenylethylene (TPE) into the molecule would improve the
solid state luminous efficiency [21]. TPE is highly emissive in solid state due to restriction of intramolecular rotation (RIR) due to twisted propeller shaped structure and also utilized for the development of AIE active mechanochromic materials [22-26]. Combination of phenanthroimidazole core with TPA and TPE units produced intriguing mechanochromic and OLED properties. Another strategy such as an asymmetrical structure has been introduced to strengthen the amorphous morphological stability and efficiency by slightly changing the substituents [26]. Recently, some progress has been made to obtain highly stable and efficient deep-blue anthracene derivatives by introducing a non-planar rotational molecular structure which efficiently interrupts $\pi$-conjugation [26].

Herein, we report, N-phenyl-N-(4-(1-(1-(4-(1,2,2-triphenylvinyl)phenyl)naphthalen-4-yl)-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl) benzenamine (TPE-NPPB) and N-phenyl-N-(4-(2-(10-(4-(1,2,2-triphenylethyl) phenyl)anthracen-9-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)phenyl) benzenamine (TPE-APPB) consist of TPA and TPE units. The AIE and mechanochromic properties of TPE-NPPB and TPE-APPB have been investigated. These excellent solid state emitters, TPE-NPPB and TPE-APPB show reversible mechanochromism between blue and green colours. The non-doped OLEDs based on TPE-NPPB and TPE-APPB fluorophores exhibit high external quantum efficiency (EQE) of 3.2 and 5.3%, current efficiency (CE) of 4.32 and 5.28 cd/A and power efficiency (PE) of 4.01 and 4.92 lm/W, respectively.

2. Experimental Section

2.1. Materials

The chemicals used in the experimental section were obtained from Sigma-Aldrich. Synthetic route of the emissive materials has been outlined in Scheme S1.

2.2. Synthesis of mechanochromic materials

(i) N-(4-(1-(1-bromonaphthalen-4-yl)-1H-phenanthro[9, 10-d]imidazole-2-yl)phenyl)-N-phenylbenzamine (BrNPPB)
A mixture of 9,10-phenanthrenequinone (2.54 mmol), 4-(diphenylamino)benzaldehyde (2.80 mmol), ammonium acetate (25.4 mmol) and 4-bromonaphthalen-1-amine (3.04 mmol) in acetic acid (10 mL) was refluxed with continuous stirring for 24 h (120°C; N₂). The resulting solid was filtered, washed with water and dried. The intermediate BrNPPB was collected as pale yellow solid. Yield: 70%. ¹H NMR (400 MHz; CDCl₃; δ, ppm): 6.68-6.54 (m, 6H), 6.58 (d, 2H), 7.03 (s, 4H), 7.21-7.24 (d, 4H), 7.41-7.50 (t, 2H), 7.69 (d, 2H), 7.85-7.89 (t, 3H), 8.12-8.20 (d, 2H), 8.91 (d, 2H). ¹³C NMR (100 MHz; CDCl₃; δ, ppm): 121.2, 122.4, 122.5, 122.6, 122.7, 122.8, 125.1, 125.2, 126.0, 126.2, 126.3, 126.4, 126.5, 126.7, 126.8, 127.0, 127.3, 127.6, 129.6, 129.8, 130.1, 131.0, 131.1, 131.3, 132.7, 141.0, 141.3, 141.4, 149.6. MS: m/z. 666.60 [M⁺]; Calcd. 666.51 (Scheme S2).

(ii) N-(4-(2-(10-bromoanthracen-9-yl)-1H-phenanthro[9, 10-d]imidazol-1-yl)phenyl)-N-phenylbenzenamine (BrAPPB)

A mixture of 9,10-phenanthrenequinone (2.54 mmol), 9-bromoanthracene-10-carbaldehyde (2.80 mmol), ammonium acetate (25.4 mmol) and N',N'-diphenylbenzene-1,4-diamine (4.32 mmol) in acetic acid (10 mL) was refluxed with continuous stirring for 42 h (120°C; N₂). The resulting solid was filtered, washed with water and dried. The intermediate BrAPPB was collected as grey coloured solid. Yield: 68%. ¹H NMR (400 MHz; CDCl₃; δ, ppm): 6.42-6.49 (m, 4H), 6.53 (d, 4H), 7.01-7.10 (m, 5H), 7.38-7.42 (m, 5H), 7.60 (t, 2H), 7.70-7.78 (m, 6H), 7.93 (d, 2H), 8.03 (d, 2H). ¹³C NMR (100 MHz; CDCl₃; δ, ppm): 118.0, 120.3, 122.6, 124.0, 125.3, 126.2, 127.2, 128.3, 129.4, 130.6, 134.8, 135.0, 140.3, 141.2, 142.6, 144.8, 148.4, 151.6, 156.4. MS: m/z. 716.66 [M⁺]; Calcd. 715.79 (Scheme S2).

(iii) N-phenyl-N-(4-(1-(4-(1,2,2-triphenylvinyl)phenyl)napthalen-4-yl)-1H-phenanthro[9, 10-d]imidazol-2-yl)phenyl)benzenamine (TPE-NPPB)

A mixture of Pd(PPh₃)₄ (0.04 mmol), BrNPPB (0.4 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester (0.52 mmol) and K₂CO₃ (2.0 mmol) in a mixture of ethanol (8.0 mL), toluene (24.0 mL) and H₂O (4.0 mL) was refluxed (120°C; N₂);
42h). The crude was purified by column chromatography. The TPE-NPPB was separated as a white powder. Yield: 65%. \(^1^H\) NMR (400 MHz, CDCl\(_3\), \(\delta\), ppm): 6.23-6.46 (m, 4H), 6.50-6.83 (t, 4H), 6.86-7.16 (m, 6H), 7.20-7.29 (m, 6H), 7.32-7.40 (m, 4H), 7.44 (t, 3H), 7.50 (s, 2H), 7.63 (s, 2H), 7.68 (t, 2H), 7.70-7.81 (m, 5H), 8.22 (s, 4H), 8.32-8.58 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\), ppm): 108.1, 122.4, 122.8, 124.7, 125.1, 126.2, 127.6, 127.8, 126.4, 126.6, 128.5, 128.4, 129.7, 131.2, 131.3, 131.5, 131.6, 134.1, 136.2, 135.8, 138.9, 140.0, 149.4. MS: m/z. 918.13 [M\(^+\)]; Calcd. 918.08 (Scheme S2).

(iv) \(N\)-phenyl-N-(4-(2-(10-(4-(1,2,2-triphenylethyl)phenyl)anthracen-9-yl)-1H-phenanthro[9, 10-d]imidazol-1-yl) phenyl) benzenamine (TPE-APPB)

A mixture of Pd(PPh\(_3\))\(_4\) (0.04 mmol), BrAPPB (0.4 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid pinacol ester (0.52 mmol) and K\(_2\)CO\(_3\) (2.0 mmol) in a mixture of ethanol (8.0 mL), toluene (24.0 mL) and H\(_2\)O (4.0 mL) was refluxed (120 \(^\circ\)C; N\(_2\); 42 h). The crude was purified by column chromatography. The TPE-APPB was separated as a white powder. Yield: 60%. \(^1^H\) NMR (400 MHz; CDCl\(_3\); \(\delta\), ppm): 6.20 (t, 4H), 6.32 (d, 4H), 6.40-6.83 (m, 4H), 6.98 (t, 3H), 7.10-7.28 (m, 6H), 7.33-7.40 (m, 6H), 7.48-7.58 (m, 5H), 7.60 (d, 4H), 7.75 (t, 3H), 7.85-8.00 (m, 4H), 8.06-8.46 (m, 6H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\); \(\delta\), ppm): 102.0, 122.5, 123.2, 123.4, 125.4, 126.5, 127.4, 128.0, 129.3, 129.7, 131.9, 133.1, 134.9, 135.0, 136.3, 137.0, 139.3, 140.5, 141.6. MS: m/z. 968.19 [M\(^+\)]; Calcd. 968.12 (Scheme S2).

2.4. Fabrication of devices

ITO glass (resistance 20 \(\Omega\)/sq) were cleaned with acetone, deionized water and isopropanol, dried (120 \(^\circ\)C) followed by UV-zone treatment (20 min) and transferred into deposition system. The devices were fabricated by the multiple source beam deposition method in vacuum at a pressure of 4\(\times\)10\(^{-5}\) mbar. Evaporation rates of 2-4 \(\AA\) s\(^{-1}\) (organic materials) and 0.1 and 4 \(\AA\) s\(^{-1}\) for LiF and metal electrodes were applied, respectively. The thickness of each deposition layer was monitored with quartz crystal thickness monitor.
The EL measurement with CIE coordinates was recorded with USB-650 VIS-NIR spectrometer (Ocean Optics, Inc, USA). The current density-voltage-luminance (J-V-L) characteristics was performed using source meter (Keithley 2450) equipped with LS-110 light intensity meter. The external quantum efficiency was determined from luminance, current density and EL spectrum assuming Lambertian distribution.

2.5. Computational details

The ground (S\textsubscript{0}) (DFT) / excited (S\textsubscript{n}*) (TD-DFT) states of emissive materials were analyzed by Gaussian 09 program [27].

3.0. Results and Discussion

3.1. Theoretical calculation

To gain more insight into the structure-activity analysis, molecular optimization and frontier molecular orbital (FMO) analysis for TPE-NPPB and TPE-APPB have been carried out by DFT and TD-DFT methods (Figures 1, S1 & S2) [27]. The optimized structures and HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbita) for TPE-NPPB and TPE-APPB are shown in Figure 1 (Table 1). The optimized structure confirm the twisted confirmation of TPE and TPA units and reveal only C-H interactions. Absence of H-bonding or \(\pi-\pi\) interactions lead to loosely packed arrangement which cause sensitive to grinding and thereby allowing mechanochromism. The twisted confirmation leads to restraint on \(\pi-\pi\) stacking interaction results in intensified emission in the aggregated form of TPE-NPPB and TPE-APPB. The optimized structures of intermediates, BrNPPB and BrAPPB reveal a propeller orientation of TPA unit. The TPA unit and bromo substituted phenyl ring in BrNPPB and BrAPPB are not in the plane of phenanthroimidazole unit and exhibit highly twisted geometry. The HOMO and LUMO are well separated in TPE-NPPB, HOMO mainly localized on phenanthroimidazole and TPA unit whereas LUMO localized on TPE unit. However, in TPE-APPB, the HOMO and LUMO are not well separated and mainly localized
on TPE and imidazole unit. The attachment of TPE unit through azomethine nitrogen atom of phenanthroimidazole in TPE-NPPB causes disruption in extended conjugation resulting in a better separation of molecular orbitals. In TPE-APPB, the TPE unit attached with carbon atom of imidazole ring producing highly extended conjugation allowing the molecular orbitals to be delocalized over whole molecule.

From the optimized molecular geometry, the π-conjugation between imidazole and anthracene in TPE-APPB is more interrupted that could induce pure blue emission. The theoretical band-gap of TPE-NPPB and TPE-APPB are of 2.12 and 2.10 eV, respectively. The computed vertical transitions, oscillator strength and HONTOs and LUNTOs of TPE-NPPB and TPE-APPB are shown in Figure S2 (Tables S1 & S2).

3.2. Mechanochromic materials

Based on theoretical calculation, design strategy have been carried out for the synthesis of TPE-NPPB and TPE-APPB by simple and efficient two step approach (Scheme 1). The intermediates, BrNPPB and BrAPPB were synthesized by the condensation reaction of 9, 10-phenanthroquinone with corresponding aldehydes, amines and ammonium acetate. The Suzuki cross-coupling reaction of BrNPPB and BrAPPB with 4-(1,2,2-triphenylvinyl) phenylboronic acid pinacol ester in nitrogen atmosphere using Pd(PPh₃)₄ catalyst yielded the target phenanthroimidazoles, TPE-NPPB and TPE-APPB with 65% and 60% yield, respectively [28].

The luminogens, TPE-NPPB and TPE-APPB were characterized by NMR and MS techniques.

3.3. Thermal and electrochemical studies

The fabrication of devices required thermally stable materials hence, the materials will be stable at elevated temperature. The thermal stability of TPE-NPPB and TPE-APPB was analysed by thermogravimetric analysis and differential scanning calorimetry (Figure 2: Table 1). The twisted molecular architecture of TPE-NPPB and TPE-APPB with twist angle ~56° between C2 substituent and phenanthrimidazole core effectively suppress the conjugation and
intermolecular π-π stacking (Figure 1). The twisted molecular architecture increased the thermal stability of TPE-NPPB and TPE-APPB. The thermal decomposition temperature ($T_d$) of TPE-NPPB (449 °C) and TPE-APPB (462 °C) implies that these materials are thermally stable and hence they are suitable choice for material applications. Compared to TPE-NPPB, the more asymmetrically twisted conformations between anthracene and imidazole units in TPE-APPB efficiently interrupt molecular π -conjugation and inhibit π-π intermolecular interactions, resulting in high thermal stability, which is important for application in devices. This geometrical morphology tends to maintain certain distance between anthracene units of adjacent molecules and suppress close packing and π-π intermolecular interactions. The DSC curve reveal an endothermic process for TPE-NPPB and TPE-APPB with high melting temperature of 273 and 320 °C, respectively. Because of C and N-side coupling with bulky substituent, rigid phenanthrimidazole show high glass transition temperature (TPE-NPPB- 261 °C; TPE-APPB- 286 °C). The interaction of substituents at C2 with N1 of phenanthroimidazole core induced more condensed molecular packing and enhanced the thermal stability which is essential for application in fabrication of devices.

The electrochemical properties and frontier energy level of TPE-NPPB and TPE-APPB were examined by cyclic voltammetry in dichloromethane using tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte. The cyclic voltammograms (Figure 2) of TPE-NPPB and TPE-APPB reveal quasi-reversible oxidation and reduction waves. The energies for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by the equations: $\text{HOMO} = -(E_{\text{onset}} + 4.4) \text{ eV}$ and $\text{LUMO} = \text{HOMO}-1239/ \lambda_{\text{onset}}$ [29]. From the calculated HOMO energy of TPE-NPPB (-5.08 eV) and TPE-APPB (-5.20 eV) and LUMO energy of TPE-NPPB (-3.01 eV) and TPE-APPB (-3.16 eV), electrochemical HOMO-LUMO gap of TPE-NPPB and TPE-APPB are found to be 2.07 eV and 2.04 eV, respectively.
3.4. Photophysical properties

Phenanthroimidazoles, TPE-NPPB and TPE-APPB are freely soluble in dichloromethane, tetrahydrofuran, chloroform and hexane but they are poorly soluble in water, alcohol and acetonitrile. The photophysical properties of TPE-NPPB and TPE-APPB were studied in tetrahydrofuran using electronic spectroscopy (Figure 3, Table 1). TPE-NPPB and TPE-APPB show absorption peaks at 243 and 249 nm, respectively, corresponding to π-π* transition of aromatic segments. The absorption peaks at 338 and 346 nm are attributed to π-π* transition of phenanthroimidazole unit [30]. The high extinction coefficient (ε_max) of TPE-NPPB and TPE-APPB is due to increase of conjugation length [TPE-NPPB: 243nm (ε_max - 41152.26 cm⁻¹ M⁻¹), 338nm (ε_max - 29585.80 cm⁻¹ M⁻¹); TPE-APPB: 249nm (ε_max - 40160.64 cm⁻¹ M⁻¹), 346nm (ε_max - 28901.73 cm⁻¹ M⁻¹)] which confirm the presence of effective charge transfer transitions in these materials [31, 32].

The photoluminance characteristics of these materials were studied in various solvents. The TPE-NPPB and TPE-APPB show emission maximum at 403 and 416 nm, respectively. The solvatochromism was examined by emission (Figure S3) and absorption spectra (Figure S4) of TPE-NPPB and TPE-APPB (Table S3 & S4). The emission spectra of TPE-NPPB and TPE-APPB in non-polar solvents display fine vibrational structure and the vibrational structure vanishes in polar solvents. The emission was red shifted in polar solvents. In non-polar solvents, the emission arises from localised excited (LE) state whereas in polar solvents, the emission originated from charge transfer (CT) state. The Lippert-Mataga plot (Figure 3) of TPE-NPPB show high slope than TPE-APPB which suggest that in TPE-NPPB, the excited state is more polarized than in TPE-APPB. The TPE moiety in these emissive materials being well established for AIE characteristics due to its propeller shape. The emission behaviour was used to study the AIE properties of TPE-NPPB and TPE-APPB (Figure 4). TPE-NPPB and TPE-APPB exhibit good solubility in tetrahydrofuran and poor solubility in water. Hence, the
gradual increase of water percentage in tetrahydrofuran solution initiates the formation of nano-aggregates. The TPE-NPPB and TPE-APPB are weakly emissive at low water fractions and the relative PLQY for TPE-NPPB and TPE-APPB are of 0.16 and 0.46, respectively. The non-radiative energy loss of the excited state caused by the free rotation of phenyl rings of TPE moiety in solution state leads to non-emissive nature [33]. The formation of aggregates at higher water percentage restricts the free rotation of phenyl ring resulting in enhanced intensity with red shifted emission. The TPE-NPPB and TPE-APPB exhibit an increase in emission intensity with bathochromic shift for above 70% water fraction due to effective aggregate formation. The TPE-APPB has higher degree of enhancement in intensity as compared to TPE-NPPB due to the positional effect. The superposition of the emission spectra of TPE-NPPB and TPE-APPB at water fraction of 90% gives intensity enhancement to higher extent (Figure S5). The AIE behaviour was also studied by using absorption spectroscopy (Figure S6). The absorption spectra for TPE-NPPB and TPE-APPB reveal a similar trend of absorption bands up to water fraction of 70%, above which there is scattering of light or Mie effect observed due to the formation of nano aggregates. The AIE behaviour of TPE-NPPB and TPE-APPB is shown in photographs under UV illumination (Figure 4).

3.5. Mechanochromism

Phenanthroimidazoles, TPE-NPPB and TPE-APPB have been analysed to display reversible mechanochromic behaviour on account of the twisted structure of TPE moiety. The mechanochromic behaviour was studied using fluorescence spectroscopy (Figure 4: Table 2). The TPE-NPPB and TPE-APPB were mechanically grinded with the aid of mortar and pestle. Pristine TPE-NPPB emits at 442 nm (sky blue) which was red shifted to 483 nm (bluish green) on grinding. The reversibility of colour switching was analysed by annealing TPE-NPPB at 230 °C for five minutes, which leads to blue emission (438 nm) with higher blue shift. The peak at 476 nm could be ascribed to intermediate species that arise from grinding of pristine
sample. These observations indicate that the highly sensitive nature of TPE-NPPB towards mechanical stimuli. The high sensitivity of TPE-NPPB could be due to the position of TPA and TPE, TPE directly attached to the nitrogen atom of imidazole ring. Similarly, pristine TPE-APPB show blue emission at 426 nm, which was red shifted to 472 nm (green) on grinding. The colour switching was analysed by annealing at 200 °C for five minutes, which leads to blue emission at 446 nm. Due to the more twisted molecular structure, the PL spectra of TPE-APPB in film exhibit a hypochromatic shift in comparison with those of TPE-NPPB. It should be noted that using 9,10-diphenylanthracene units to substitute at C-2 position of phenanthrimidazole can efficiently limit the π-conjugation, which induces deep-blue emission.

The absolute quantum yield for TPE-NPPB in its pristine, grind and annealed forms are of 48.63%, 51.08% and 66.93%, respectively. The absolute quantum yield for TPE-APPB in its pristine, grind and annealed forms are of 69.03%, 78.92% and 81.03%, respectively. The TPE-NPPB and TPE-APPB exhibit grinding induced spectral shift of 45 and 26 nm, respectively.

The powder XRD (PXRD) studies of TPE-NPPB and TPE-APPB have been performed to gain insight into the morphological change that could be a possible reason associated with reversible mechanochromic behaviour (Figure 5). The pristine TPE-NPPB and TPE-APPB displayed sharp and intense diffraction peaks attributed to crystalline structures. The sharp diffraction peak disappear on grinding giving a broad band which implies that the morphological change from crystalline state to amorphous state. The crystallinity of TPE-NPPB and TPE-APPB is resumed on annealing which is clearly seen by the sharp diffraction peaks.

3.6. Electroluminescent studies

In view of excellent thermal stability, AIE character and high PLQY in solid state, TPE-NPPB and TPE-APPB have been employed as emissive layers to fabricate non-doped OLEDs with configuration of ITO/ HATCN (1,4,5,8,9,11 hexaazatriphenylenehexacarbonitrile) (5 nm)/ NPB (N,N’-bis(phenyl)-benzidene) (40 nm)/ TPE-NPPB and TPE-APPB (20 nm)/ TPBi
(1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene) (40 nm)/ LiF (1 nm)/ Al [HATCN- hole injection layer, NPB- hole transporting layer and TPBi- electron transporting layer] (Figure 6).

Figure 7 shows the current density and luminance of non-doped devices with TPE-NPPB and TPE-APPB as emissive layer. The small difference of current density and luminance reveal that the positional change of TPA and TPE units in the backbone structure does not affect the carrier transport properties of the emitters. The turn-on voltage of the devices were same because of small difference of carrier injection from carrier transport layers to emissive layer.

The non-doped devices based on TPE-NPPB and TPE-APPB exhibit blue emission of 444 and 428 nm, high external quantum efficiency (EQE) of 3.2 and 5.3 %, current efficiency (CE) of 4.32 and 5.28 cd/A, power efficiency (PE) of 4.01 and 4.92 lm/W and luminance of 10231 and 15461 cd/m$^2$, respectively. Compared TPE-NPPB (0.18, 0.21), the device using TPE-APPB as a blue emitter shows a purer blue emission with CIE coordinates of (0.18, 0.19) which could be attributed to the fully twisted molecular structure. The performance of non-doped devices indicates that the asymmetrically twisted molecular structure can efficiently suppress the π-π intermolecular interaction between the adjacent molecules and result in deep-blue emission.

The TPE-NPPB and TPE-APPB based devices exhibit high EQE because of AIE character which suppresses concentration quenching. The EQE of TPE-APPB based devices was high because of strong AIE behaviour as confirmed in the PL intensity change by the addition of water fraction. The efficient AIE property of TPE-APPB contributed to high EQE in non-doped OLEDs. The non-doped devices based on TPE-NPPB and TPE-APPB exhibit low efficiency roll-off and their EQE can still remain 3.15 % and 5.25 % at a brightness of 1000 cd m$^2$. All devices show negligible - roll off efficiency (TPE-NPPB1.45-% and TPE-APPB-0.94 %) due to suppression of current induced exciton quenching and effective h$^\text{+}$-e$^\text{-}$ recombination. The high EQE and low roll-off efficiency further emphasized a great potential of these materials for industrial applications.
The EL spectra of TPE-APPB based device were shifted to shorter wavelength, which is in agreement with the relative PL peak position of the two emitters. Compared with TPE-NPPB, anthracenyl substituted TPE-APPB show bathochromic shift due to conjugation [26]. Relatively broad emission modification strategy can be used as mechanochromism managing tool while maintaining EL performances.

**Conclusion**

We have designed positional isomers of phenanthroimidazoles TPE- NPPB and TPE-APPB consist of TPE and TPA unit and synthesized by Suzuki cross-coupling reaction. The DFT studies reveal better separation of HOMO and LUMO in TPE-NPPB compared to TPE-APPB which is attributed to the positions of TPE and TPA units. The thermally stable TPE-NPPB and TPE-APPB isomers display strong AIE characteristics and exhibit reversible emission in response to mechanical stimuli with excellent colour contrast. The isomer TPE-NPPB show high sensitivity towards mechanical stimuli as relative to TPE-APPB. The PXRD pattern reveal that the observed morphological change from amorphous state to crystalline state is associated with colour changes. The coupling of TPA and TPE to phenanthroimidazole backbone provides a new approach for the development of stimuli responsive solid state emitters. The non-doped device based on TPE-APPB exhibits high external quantum efficiency (EQE) of 5.3 %, current efficiency (CE) of 5.28 cd/A, power efficiency (PE) of 4.92 lm/W and luminance (L) of 15461 cd/m² (Table 3). The coupling of phenanthroimidazole, TPA and TPE synergistically leads to high solid state emission which can be further employed in optoelectronic applications.
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Figure 1. Molecular structure, optimized geometry and frontier molecular orbitals (FMO) of TPE-NPPB and TPE-APPB.
**Figure 2.** (a) TGA and DSC graph and (b) Cyclic voltammogram of TPE-NPPB and TPE-APPB.
Figure 3. (a) Normalised absorption and emission spectra and (b) Lippert-Mataga plot of TPE-NPPB and TPE-APPB.
Figure 4. Emission spectra of (a) TPE-NPPB and (b) TPE-APPB in THF-H$_2$O with different water fractions; (c) UV illumination of TPE-NPPB and TPE-APPB in THF-Water mixtures with different water fractions (10 µM) (0% to 90% water fraction from L to R) and (d) Emission spectra of pristine, grind and annealed solids of TPE-NPPB and TPE-APPB.
Figure 5. Powder X-ray diffraction and mechanochromic behaviour of (a) TPE-NPPB and (b) TPE-APPB.
Figure 6. Non-doped device configuration with energy level of TPE-NPB and TPE-APPB.
Figure 7. Device performances: (a) Luminance- Current density - Voltage; (b) External quantum efficiency - Current density (c) Current efficiency - Current density; (d) Power efficiency - Current density and (e) Normalized EL spectra of TPE-NPPB and TPE-APPB.
Table 1. Summary of optical and thermal properties.

| Properties       | TPE-NPPB       | TPE-APPB       |
|------------------|---------------|---------------|
| $T_d$ / $T_g$ / $T_m$ (°C) | 449/261/273   | 462/286/320   |
| $\lambda_{ab}$ (nm)    | 243,338       | 249,346       |
| $\lambda_{em}$ (nm)     | 403           | 416           |
| $\Phi$ (soln)         | 0.16          | 0.46          |
| HOMO/LUMO (eV)        | -5.08/-3.01   | -5.20/-3.16   |
| $E_g$ (eV)            | -2.07         | -2.04         |

Table 2. Emission behaviour of TPE-NPPB and TPE-APPB under external stimuli.

| Compounds | $\lambda_{pristine}$ | $\lambda_{grind}$ | $\lambda_{annealed}$ | $\Delta\lambda$ |
|-----------|----------------------|-------------------|----------------------|-----------------|
| TPE-NPPB  | 442                  | 483               | 438                  | 45              |
| TPE-APPB  | 426                  | 472               | 446                  | 26              |

Table 3. Electroluminescent efficiency of TPE-NPPB and TPE-APPB based devices.

| Emitters | CE (cd/A) | PE (lm/W) | EQE (%) | L (cd/m²) | EL (nm) | CIE (x,y) |
|----------|-----------|-----------|---------|-----------|---------|-----------|
| TPE-NPPB | 4.32      | 4.01      | 3.2     | 10231     | 444     | 0.18, 0.21|
| TPE-APPB | 5.28      | 4.92      | 5.3     | 15461     | 428     | 0.18, 0.19|