Efficient Non-Doped Deep Blue Organic Light Emitting Diodes with High External Quantum Efficiency and a Low Efficiency Roll-off Based on Donor-Acceptor Molecules

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Abstract:

Two phenanthroimidazole derivatives containing carbazole and pyrene units were designed and synthesized. Highly efficient non-doped deep blue organic light emitting diodes (OLEDs) were fabricated by using these materials as emissive layer. The non-doped devices demonstrated high efficiency (4.24 cd/A, 3.67 lm/W, 4.66%), low efficiency roll-off at higher current densities, and stable deep blue emissions with CIEy around 0.10, which are excellent results for deep-blue OLED devices. This study reveals that the combination of phenanthroimidazole and donor-linker-acceptor strategy has a great potential for developing high performance deep-blue OLEDs.

Keywords: Blue emission, phenanthroimidazole, pyrene, carbazole, non-doped, OLEDs

1. Introduction

Organic light emitting diodes (OLEDs) have attracted much attention in the past decades for their promising application potentials in flat panel display and solid-state lighting resources. Recently, blue OLEDs have gained a lot of scientific and industrial interest because of their short life time and low efficiency compared to the green and red ones [1]. Blue emission not only decreases the power consumption but it also produces emission of other colors through cascade energy transfer mechanism [2], whereas highly efficient and stable deep blue emitters are still deficient [3-4]. Several phosphorescent and thermally activated delayed fluorescence (TADF) materials with excellent performance are developed which can achieve 100% IQE [5-7]. However, a very less number of these materials fulfills the requirement of deep blue emitters with Commission International de L'Eclairage (CIE) coordinates of $y < 0.08$, which meets the National Television System Committee (NTSC) standard blue CIE of (0.14, 0.08) [8-11]. A difficulty in the synthesis of efficient phosphor is the non-radiative decay through the metal d-orbitals during metal-ligand charge transfer (MLCT) band into deep blue region [12-13]. Due to intramolecular charge transfer (ICT), TADF materials show broad emission, leading to a decrease in color purity [14]. So, development of efficient novel deep blue emitters is still of great importance.

In spite of high efficiency, host-guest system has some major drawbacks. For instance, the phase separation could diminish the device performance badly during operation. Apart from this, it requires the additional further design of good hosts is required which makes it difficult to evaluate the blue emitters. In view of this, use of non-doped emissive materials are a rational

approach for OLED applications. Several attempts have been made to explore different types of non-doped blue fluorescent emitters, for instance anthracene, fluorene, spirobifluorene, di(styryl)arylene, and pyrene containing molecules to enhance their electroluminescence (EL) performances [15-18]. For example, Adachi and co-workers developed 9,10-diphenylanthracene which is also used as a standard to measure the photoluminescent quantum yield (PLQY) because its fluorescence quantum efficiency is near one in dilute solution [19]. But, its fluorescence is easily quenched due to aggregation in the solid state.

Another approach to synthesize efficient non-doped blue emitters is the introduction of bulky side chain in the emission core. By this way, fluorescence quantum yield of the material is increased in the thin film state. With this idea, different hydrocarbons with steric hindrance were attached to the anthracene core to obtain non-doped blue emitters [16,18]. Apart from good thermal stability and ability to reduce the close packing in film, good charge injection and charge transporting properties for balanced charge recombination are also required to develop high performance non-doped blue emitters. Different groups with good charge transport ability were incorporated into the molecules to improve its charge transport properties [20-21]. Non-doped blue emissive materials with high PLQY, restricted intermolecular interactions, and good charge injection as well as charge transporting abilities are demanded to obtain stable and efficient blue OLED devices.

Besides this, there is one more obstacle that restricts the commercialization of OLEDs is the significant efficiency roll-off at higher current densities. Both, phosphorescent and TADF materials exhibit this effect because of triplet-triplet annihilation (TTA) process [22-23]. It is also reported that many efficient fluorophores also show significant efficiency roll-off, which is due to the reduction of carrier confinement at high current densities and unbalanced charge

carrier mobility [24-26]. Consequently, the deep blue material with a balanced ambipolar property is urgently required to reduce the efficiency roll-off.

Imidazole is an asymmetric aromatic heterocyclic compound containing two nitrogen atoms with different points of bonding and ambipolar nature [27-28]. Imidazole based materials have demonstrated excellent performances in optoelectronic applications [29-30], not only used as electron transport materials, 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene (TPBi), but also as efficient emissive layers, (BTPE-PI, PhBPI) [31-37]. Interestingly, these materials show quite low efficiency roll-off. Apart from benzimidazole and phenanthrene imidazole based, some pyrene containing blue imidazole emitters have some potential for applications in optoelectronic field [38-39]. Carbazole is one of those few molecules which have high triplet energy level (E_T) and sufficient HT property, whose derivatives are considered as the good candidates for blue phosphorescent host materials. Pyrene is a blue-light-emitting compound containing four fused benzene units, which is a very promising building block for OLEDs because of its features such as good chemical stability, high charge mobility, and excellent hole injection ability along with high photoluminescence efficiency and high charge carrier mobility [40-41]. Importantly, pyrene itself does not work well as blue-emitter in OLEDs because it forms excimers, resulting in a red-shifted emission with a decrease in the fluorescence intensity. This property has restricted the use of pyrene as an emissive material in OLEDs. Hence, many efforts in the structural modification of pyrene containing emissive materials have been made to suppress aggregation and increase the fluorescence quantum yield for OLEDs application.

Herein, to synthesize efficient blue emissive materials, we have developed two novel phenanthroimidazole emitters containing pyrene and carbazole, N,N-diphenyl-4'-(1-(3-(9-phenyl-9H-carbazol-3-yl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)biphenyl-4-amine

(TPACzPI) and N,N-diphenyl-4'-(1-(3-(pyren-1-yl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)biphenyl-4-amine (TPAPyPI). These materials exhibit high thermal stability with good charge carrier properties. Non-doped OLEDs fabricated by using TPACzPI or TPAPyPI as emitting layers showed stable deep blue emission with CIEy around 0.08, high efficiency (4.24 cd/A, 3.67 lm/W, 4.66%) and a low efficiency roll-off. These results have indicated that the combination of imidazole and donor- π -acceptor can provide a good strategy to develop stable and highly efficient deep blue emitters for OLEDs.

2. Experimental Section

2.1. General Methods

Nuclear magnetic resonance (^1H NMR) and (^{13}C NMR) spectra were carried out on a Bruker DRX-400 spectrometer. ESI-MS spectra were studied with an FINNIGAN Trace DSQ mass spectrometer at 70 eV. Elemental analyses were investigated with a Perkin Elmer 2400 II elemental analyzer. UV/vis absorption spectra were measured on a Perkin Elmer Lambda 950 spectrophotometer. Photoluminescent (PL) spectra were measured with a FLSP920 spectrophotometer. Thermogravimetric analyses (TGA) were explored using a Perkin Elmer Pyris thermogravimeter at $10^\circ\text{C min}^{-1}$ using nitrogen atmosphere. Cyclic voltammetry (CV) measurements were recorded on a CHI 660D electrochemical workstation using a Pt disk as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode, in a dichloromethane solution containing 0.1 M of tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

2.2. Synthesis of the Compounds

Phenanthrene-9,10-dione (**1**), 9-phenyl-9H-carbazol-3-ylboronic acid (**4**), pyren-1-ylboronic acid (**5**), 3-bromoaniline were purchased from TCI co. 4'-(diphenylamino)biphenyl-4-carbaldehyde (**2**) was prepared according to the reported method [42].

Scheme 1. The synthetic route to TPA-CzPI, TPA-PyPI.

2.2.1. Synthesis of 4'-((1-(3-bromophenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)-N,N-diphenylbiphenyl-4-amine (3):

4'-(diphenylamino)biphenyl-4-carbaldehyde (1.0 mmol), 0.208 g of phenanthrene-9,10-dione (1.0 mmol), 0.40 g of ammonium acetate (5.0 mmol), 0.85 g of 3-bromoaniline (5.0 mmol), and acetic acid (10 mL) were put into a flask and refluxed under nitrogen. After about 12 h, the reaction was stopped and cooled, and the mixture was added 50 mL of water and filtered. The precipitates were dissolved in dichloromethane and dried over anhydrous MgSO_4 . The product was purified by column chromatography. ^1H NMR (400 MHz, CDCl_3): δ 8.90 (d, J = 8, 1H), 8.79 (d, J = 8, 1H), 8.72 (d, J = 8, 1H), 7.75-7.82 (m, 3H), 7.63-7.71 (m, 3H), 7.49-7.57 (m, 7H), 7.27-7.36 (m, 5H), 7.20 (d, J = 8, 1H), 7.14 (d, J = 8, 6H), 7.04 (t, J = 8, 2H).

2.2.2. Synthesis of Compound **TPA-CzPI**:

Compound **3** (0.5 mmol), 9-phenyl-9H-carbazol-3-ylboronic acid (**4**) (1 mmol), and 50 mg of $\text{Pd(PPh}_3)_2\text{Cl}_2$ (0.1 mmol) were added in the solution of 30 mL of THF and 10 mL of 2M K_2CO_3 , and the mixture was heated to 80 °C and stirred for overnight under nitrogen. After cooling, the mixture was extracted by using dichloromethane (40 mL $\times$ 3 times), washed by using water (10 mL $\times$ 3 times), and dried with anhydrous MgSO_4 . The product was purified by silica gel column chromatography with dichloromethane–petroleum ether as an eluent, a white solid was obtained. Yield: 70%. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (d, J = 8, 1H), 8.83 (d, J = 8, 1H), 8.74 (d, J = 8, 1H), 8.35 (s, 1H), 8.12 (d, J = 8, 1H), 8.01 (d, J = 8, 1H), 7.93 (s, 1H), 7.42-7.79 (m, 22H), 7.25-7.36 (m, 6H), 7.10-7.14 (m, 6H), 7.03-7.06 (t, 2H). ^{13}C NMR (400 MHz, CDCl_3) δ 150.71, 147.57, 144.10, 141.46, 140.89, 140.79, 139.19, 137.42, 133.92, 131.38, 130.51, 129.98, 129.87, 129.43, 129.35, 129.29, 128.43, 128.36, 128.12, 127.70, 127.66, 127.56, 127.05, 126.83, 126.44, 126.40, 126.31, 125.70, 125.22, 124.98, 124.50, 124.17, 124.04, 123.73, 123.21, 123.09, 123.04,

122.96, 121.08, 120.45, 120.28, 118.94, 110.29, 110.01. HRMS (MALDITOF), m/z : 855.30 (M^+)

2.2.3. Synthesis of Compound **TPA-PyPI**:

Compound **3** (0.5 mmol), 1-pyreneboronic acid (**5**) (1 mmol), and 50 mg of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.1 mmol) were added in the solution of 30 mL of THF and 10 mL of 2 M K_2CO_3 , and the mixture was heated to 80 °C and stirred for overnight under nitrogen. After cooling, the mixture was extracted by using dichloromethane (40 mL×3 times), washed by using water (10 mL ×3 times), and dried with anhydrous MgSO_4 . The product was purified by silica gel column chromatography with dichloromethane–petroleum ether as an eluent, a white solid was obtained. Yield: 70%. ^1H NMR (400 MHz, CDCl_3): δ 8.96 (s, 1H), 8.83 (d, $J = 8$, 1H), 8.74 (d, $J = 8$, 1H), 8.19-8.22 (m, 2H), 8.07-8.12 (m, 3H), 7.98-8.02 (m, 2H), 7.75-7.92 (m, 10H), 7.67 (d, $J = 8$, 3H), 7.57-7.62 (m, 4H), 7.44 (t, $J = 8$, 1H), 7.27-7.32 (m, 6H), 7.17-7.20 (m, 6H), 7.05 (t, $J = 8$, 2H). ^{13}C NMR (400 MHz, CDCl_3) δ 150.88, 147.71, 147.59, 143.58, 141.06, 140.98, 138.63, 135.44, 133.93, 131.82, 131.38, 131.12, 131.08, 130.75, 130.23, 130.15, 129.46, 129.41, 129.34, 128.44, 128.33, 128.09, 128.02, 127.92, 127.78, 127.32, 127.30, 126.43, 126.36, 126.14, 125.71, 125.41, 125.05, 124.86, 124.75, 124.69, 124.63, 124.56, 124.22, 123.79, 123.68, 123.39, 123.12, 123.03, 122.94, 121.05; HRMS (MALDITOF), m/z : 814.20 (M^+).

2.3. Device Fabrication and Characterization

Before the fabrication of OLEDs, sublimation of the compounds TPA-CzPI and TPA-PyPI were performed with the first pipe heating up to 360°C for purification. The ITO-coated glass substrates were washed as usual with different solvents and then treated with UV-ozone for 15 min. The OLED devices were constructed with the structure of ITO/HAT-CN(5 nm)/NPB (40

nm)/TAPC (10 nm)/TPA-CzPI or TPA-PyPI (30 nm)/TPBi (40 nm)/LiF (1 nm)/Al (150 nm) (devices A and B). All the organic and inorganic layers were deposited in sequence at 10^{-6} Torr with the deposition rate of $0.9\text{--}1.1 \text{ \AA s}^{-1}$. The electroluminescence spectra and the Commission Internationale del'Eclairage coordination of the device were tested on a PR655 spectra scan spectrometer. The luminance-current and density-voltage characteristics were measured simultaneously from the measurement of the EL spectra by combining the spectrometer with a Keithley 2400 programmable voltage-current source. All measurements were conducted at room ambient conditions.

3. Results and Discussions

3.1 Synthesis

Scheme 1 illustrated the synthesis of TPA-CzPI and TPA-PyPI. Our design of the phenanthroimidazole based compounds was inspired by the twisted structure of phenanthroimidazole derivatives, widely used materials for fluorescent OLEDs that exhibit good blue emission [42]. To enhance the family of twisted phenanthroimidazole-based molecules with high performance of OLEDs, we adopted phenanthroimidazole and its derivatives as the central core to form twisted structure. Apart from this, recently we have also reported similar type of materials with extension of conjugation through hybrid local and charge transfer mechanism [37]. So, based on our previous work, two novel twisted phenanthroimidazole derivatives were designed with the same building blocks but different side chain moieties. As shown in Scheme 1, for the synthesis of these materials, an important intermediate compound (**3**) was prepared by the condensation of phenanthrene-9,10-dione, 4'-(diphenylamino)biphenyl-4-carbaldehyde and 3-bromoaniline. Both compounds, TPACzPI and TPAPyPI were easily synthesized in high yield (more than 70%) through suzuki coupling reaction of compound **3** with 9-phenyl-9H-carbazol-3-

ylboronic acid (**4**) or pyrene-boronic acid (**5**), respectively. All the compounds were characterized by ^1H and ^{13}C NMR spectrometry as well as mass spectrometry.

3.2. Electrochemical Properties

The electrochemical behavior of both the materials was studied by cyclic voltammetry (CV). The HOMO energy levels of the materials were determined from the onset potential of the first oxidation relative to ferrocene (Fig. 1). The first oxidation event was observed at 0.457 and 0.436 eV (vs.Fc/Fc⁺). HOMO values are obtained from the formula of $E_{\text{HOMO}} = -([E_{\text{onset}}]_{\text{ox}} + 4.8)$. The values of TPACzPI and TPAPyPI are -5.01 and -4.99 eV, respectively. These HOMO energy levels are comparatively lower than the work function of ITO, which can significantly decrease the hole injection barrier into the emission layer and enhance the device efficiency [44]. The energy band gaps (E_g) of TPACzPI and TPAPyPI were calculated to be about 3.03 eV for each material, which are determined from the onset of UV-vis absorption spectra. Finally, the LUMO levels of TPACzPI and TPAPyPI were found to be -1.99 and -1.96 eV. The results are summarized in Table 1.

Fig. 1. Cyclic voltammogram curve of TPA-CzPI and TPA-PyPI.

3.3. Thermal Properties

The thermal properties of TPACzPI and TPApyPI were investigated with TGA under a nitrogen atmosphere as shown in Fig. 2, and their thermal data are summarized in Table 1. The TGA measurement shows that both derivatives possess high thermal stabilities of more than 500°C. A weight loss of 5% (T_d) is observed at 528°C for each material. This value is 100°C higher than the sublimation temperature and indicates the high thermal stability of these materials.

Fig. 2. TGA curves of TPA-CzPI and TPA-PyPI

3.4. Theoretical Calculations

To gain insight into the electronic structures of the compound, the ground-state geometries and the frontier molecular orbital energy levels were calculated using the density functional theory (DFT) in Gaussian 03 program at the B3LYP/6-31G (d) level. Both molecules are the derivatives of TPA-PPI [42], which has a twisted geometrical configuration. So, in this twisted geometry, there is a chance of overlapping of molecular orbitals to form a hybrid local and charge transfer state. From Fig. 3 (a), the calculated highest occupied molecular orbital (HOMO) of TPA-CzPI is found to be mainly distributed on the TPA moiety, phenyl linker and partly on the phenanthroimidazole moiety. Whereas the lowest unoccupied molecular orbital (LUMO) of TPACzPI is found to be mainly populated on the phenanthroimidazole moiety, phenyl linker and to some extent on TPA moiety as well (Fig. 3b). This result suggests that carbazole moiety does

not contribute much to HOMO/LUMO levels in this molecule. On the other hand, the HOMO level of TPAPyPI is found to be mainly distributed on the TPA moiety, phenyl linker and partly on the phenanthroimidazole moiety (Fig. 3c). However, the LUMO level of TPAPyPI is localized on the pyrene moiety (Fig. 3d). The HOMO and LUMO levels of TPAPyPI are well separated. The HOMO and LUMO energy levels of TPACzPI are calculated to be -4.85 and -1.18 eV, respectively, whereas The HOMO and LUMO energy levels of TPAPyPI are calculated to be -4.92 and -1.72 eV, respectively. Low LUMO levels of both the materials are expected to be responsible for low efficiency of the devices.

Fig. 3. Structures and HOMO LUMO levels of TPA-CzPI (a & b) and TPA-PyPI (c & d).

3.5. Photophysical Properties

TPACzPI and TPAPyPI exhibited good solubility in common organic solvents like tetrahydrofuran (THF), dichloromethane, chloroform, etc., but were not soluble in water and methanol due to the presence of hydrophobic aromatic units. The UV-vis absorption and PL spectra of TPACzPI and TPAPyPI in solution are shown in Fig. 4, and the photophysical parameters are summarized in Table 1. The absorption spectra of both materials show two peaks at 296 nm, 360 nm, 286 nm and 346 nm, respectively. The absorption bands in the region from 250 to 300 nm might originate from a combination of π - π^* transitions of the aromatic segments [45]. The absorption peaks at 360 nm and 346 nm can be attributed to the delocalized π - π^* transition of the phenanthroimidazole [45]. The emission spectra of TPACzPI and TPAPyPI is quite similar and gives blue emission at 441 nm and 442 nm in the solution, individually, which is very similar to their parent deep blue emitter TPAPPI (438 nm) [42]. From the onset of absorptions, the optical band gaps (E_g) of TPACzPI and TPAPyPI were estimated to be 3.03 eV of each, subsequently.

Fig. 4. UV-vis absorption and PL spectra of TPA-CzPI and TPA-PyPI in dilute THF solution.

Table: 1. Thermal properties, optional properties and energy levels of TPACzPI and TPAPyPI.

Compound	Abs. ^a (nm)	PL ^a (nm)	T _d ^b (°C)	HOMO (eV ^c , eV ^d)	LUMO (eV ^c , eV ^d)	E _g ^e (eV)	E _g ^f (eV)
TPACzPI	296, 360	441	521	-5.01/-4.85	-1.99/-1.18	3.03	3.67
TPAPyPI	286, 346	442	529	-4.99/-4.92	-1.96/-1.72	3.03	3.20

^a Measured in THF solution.

^b Estimated based on absorption onset and cyclic-voltammetry.

^c DFT calculation with B3LYP/6-31G.

3.6. Electroluminescence Properties

EL properties of TPACzPI and TPAPyPI were finally investigated to prove its applicable feasibility. Non-doped devices were fabricated using a device structure of ITO/HAT-CN (5 nm)/NPB (40 nm)/TCTA or TAPC (10 nm)/TPACzPI or TPAPyPI (30 nm)/TPBi (40 nm)/LiF (1 nm)/Al (150 nm) (devices A and B), where 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN) and LiF were used to improve hole and electron injection of ITO (indium tin oxide) anode and Al cathode interface, respectively, N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (NPB) and 4,4',4''-tri(N-carbazolyl)-triphenylamine (TCTA) or 1,1'-bis(di-4-tolyl-aminophenyl)cyclohexane (TAPC) were utilized as the hole transporting layers (HTL), while 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBi) employed as the electron transporting (ETL) and hole-blocking layer (HBL).

Fig. 5 presents the current density-voltage-luminance (J-V-L), at the same current densities, TPAPyPI shows stronger fluorescence, resulting in higher efficiency compared to TPACzPI. The two fluorescent emitters also show great balance between high efficiency and high luminance, i.e., the efficiency roll-off of CE and EQE are very low as shown in Fig.6 & 8. This small efficiency roll off is ascribed to the ambipolar nature of these derivatives. The performance data of all the devices are listed in Table 2. For non-doped devices, A1 and B1 using TCTA as EBLs, TPACzPI and TPAPyPI exhibited unaltered emission peaks at 434 nm and 440 nm and the full width at half-maximum (FWHM) values are located at 55.3 and 55.8 nm, respectively (as shown in Fig. 4), with CIE coordinates of (0.153, 0.087) and (0.151, 0.082), which are very close to the European Broadcast Union (EBU) television blue emission (EBU, 0.150, 0.060). Moreover, the

devices reach maximum EQEs of 3.62% and 3.99% with TPACzPI and TPAPyPI as emitter, respectively, which are among the excellent efficiencies of deep blue devices [46-49].

Fig. 5. Current density-voltage-luminance (J-V-L) characteristics of non-doped devices A and B.

Fig. 6. Current efficiencies versus luminance and EQEs versus luminance characteristics of devices.

To achieve better device performance, TAPC (device A2 & B2) was used as EBL instead of TCTA (device A1 & B1) to fabricate non-doped device with TPAPyPI. The low-lying LUMO of TCTA is likely to cause electrons diffusing from the emissive layer, which is the primary cause of low efficiencies. The high-lying LUMO and higher triplet energy ($T_1=2.98$ eV) of TAPC compared to TCTA can confine more excitons and blocking electrons from diffusing into the HTL. The high-lying HOMO of TAPC (5.4 eV) compared with TCTA (5.7 eV) will decrease the injection barrier between NPB/EBL interface and achieve a better energy level alignment. As the J-V characteristics (Fig. 5) shows, the device using TAPC as EBL can get higher current densities under lower driving voltage. However, the steeper increment under higher driving voltage indicates more charge carriers are injecting into the adjacent HTLs. Overall, TAPC can maintain high current density at low driving voltage, while blocking electrons diffusing into NPB. Positively, the EL (Fig. 7) of TPAPyPI device B2 remain nearly identical to TPAPyPI device B1 and exhibited excellent deep blue light with a CIE coordinate of (0.1454, 0.1367). As expected, the EQE increased from 3.99% to 4.66%, and the PE was also increased. Furthermore, device B2 maintain high EQE of 4.39% even at a bright luminescence of 1000 cd m^{-2} . On the other hand, the EL (Fig. 7) of TPACzPI device A2 remain nearly identical to TPACzPI device A1 also and exhibited excellent deep blue emission with a CIE coordinate of (0.159, 0.095). However, surprisingly, the EQE of TPACzPI device A2 is decreased from 3.62% to 3.11% (device A1). But overall, the performance of TPAPyPI based devices is much better than TPACzPI devices. This is attributed to the high photoluminescence quantum yield of pyrene based derivatives, leading to the high efficiencies of the devices. A low efficiency roll-off is found in the devices because of comparatively balanced charge carrier mobility at higher current

density and better exciton confinement in the recombination zone (emissive layer). The non-doped device performances of these materials are better than many similar molecules such as; PPI, TPA-PIM, TPA-PPI, PyINA [46-49]. Comparison of these results with the reported ones clearly demonstrate the significant improvement not only in $PE_{\max}$ but in $EQE_{\max}$ as well. From the device performance of these emitters, we can expect that by the extension of chain length at the phenyl ring of TPA-PPI with fused ring units, efficient derivatives of TPA-PPI could be obtained with superior device efficiency.

Fig. 7. EL spectra at a current density of 5 mA/cm².

Fig. 8. Power efficiency versus current density characteristics of devices.

Table 2: Electroluminescence Data of the devices.

Compound	V_{on}^a (V)	CE_{max}^b (cd/A)	PE_{max}^c (lm/W)	EQE_{max}^d (%)	EL λ_{max}^e (nm)	CIE^f (x, y)	EQE at 100/1000 cd/m ²
PPI ⁴⁶	3.8	0.71	0.40	1.86	412	(0.161, 0.065)	-
TPA-PIM ⁴⁷	-	1.14	0.79	3.28	420	(0.161, 0.046)	316/3.11
TPA-PPI ⁴⁸	-	5.66	6.13	5.02	434	(0.15, 0.11)	3.76
PyINA ⁴⁹	2.9	2.62	-	3.68	440	(0.157,	3.61/3.66

						0.084)	
A1	3.67	2.84	3.02	3.62	434/55.3	(0.15, 3.43/2.81 0.08)	
A2	3.20	2.64	2.61	3.11	434/55	(0.15, 3.05/2.70 0.09)	
B1	4.12	3.12	3.15	3.99	440/55.8	(0.15, 3.81/3.30 0.08)	
B2	3.36	4.24	3.67	4.66	440/55	(0.14, 4.64/4.39 0.13)	

^a Driving voltage measured at 100 cd m⁻². ^b Maximum current efficiency. ^c Maximum power efficiency. ^d Maximum external quantum efficiency. ^e EL peaks. ^f Commission International de l'Eclairage coordinates measured at a driving voltage of 5 V. ⁴⁶⁻⁴⁹ References.

4. Conclusions

In summary, we have designed and prepared high performance deep-blue phenanthroimidazole derivatives. Different moieties, such as carbazole and pyrene were attached to phenyl group of phenanthroimidazole to increase the triplet energy level and photoluminescence quantum yield. The obtained two deep-blue emitters were utilized as emissive layers in OLEDs. The devices based on these emitters exhibited low turn-on voltages (as low as 3.67 V), high efficiency (4.24 cd/A, 3.67 lm/W, 4.66%), comparatively small efficiency roll-off at higher current densities, and stable deep blue emissions with CIEy < 0.10. These are among the excellent results reported so far for deep-blue OLED devices using phenanthroimidazole and pyrene based materials. The results demonstrate a promising

combination of phenanthroimidazole and the donor- π -acceptor to develop efficient deep blue emitters.

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