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### **Credit author statement**

Jaipal Devesing Girase and Jairam Tagare carried out all experiments including synthesis, structural characterization, photophysical, electrochemical, computational study and wrote manuscript. Shahnawaz, Mangey Ram Nagar and Iram Siddique: OLED fabrication, characteristation and analysis, Data Curation and wrote manuscript. Jwo-Huei Jou: OLED device design, Supervision, Writing – review & editing, Sabita Patel: Supervision, Writing – review & editing, Sivakumar Vaidyanathan: Conceptualization, Methodology, Validation, Supervision, Writing – review & editing, Funding acquisition.

Journal Pre-proof

# Deep-blue emitters (CIEy ~0.07) based on phenanthroimidazole: Remarkable substitution effects at the N1 position of imidazole on the excited states and electroluminescence properties

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## TOC



### Abstract:

Organic light emitting diodes (OLEDs) has shown great potential (light weight, fast response time, flexible and energy efficient) and emerging technology for next-generation display and lighting application. In any case, achieving efficient blue electroluminescence still remains a challenge. Herein, two new deep blue phenanthroimidazole (A) and triphenylamine (D) based fluorophores, N,N-diphenyl-4'-(1-(p-tolyl)-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1'-biphenyl]-4-amine (4-PIPTPA) and N,N-diphenyl-4'-(1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10d]imidazol-2-yl)-[1,1'-biphenyl]-4-amine (4-PIPCFTPA) were designed and synthesized. The fluorophores were structurally characterized by spectroscopic methods. These fluorophores are tharmally stable with thermal decomposition temperature ( $T_d$ ) of ~446 °C. The photophysical, electronic (theoretical), electrochemical (CV), and electroluminescene properties were thoroughly investigated, the N1 substituted moieties are play a vital role as it affects the photophysical as well as electronic proprties of the synthesized fluorophores. Hence, we fabricated undoped and doped devices with newly synthesized emitters and observed that the 4-**PIPCFTPA** demonstrated the superior performance as compared to that of **4-PIPTPA**. The best electroluminescence performance is displayed by the device fabricated with 4-PIPCFTPA (1 wt% in the CBP host) and (3 wt% in the CBP host) with a maximum external quantum efficiency (EQE) of 2.7 and 2.9%, respectively and CIE coordinates of (0.17, 0.07) and (0.18, 0.12) were observed, respectively. The observed EL properties of emitters reveal its potential as efficient deep blue emitters for display applications.

Keywords: phenanthroimidazole, Blue emitters, OLED, NTSC standard,

### Introduction

The remarkable evolution in the field of organic electronic devices were perceived from last two decades, has been to a great extent accomplished due to successful advancement of facile and economical approaches to various aromatic organic materials, demonstrating a range of tunable physical properties[1][2]. For the commercial applications of OLEDs as well as in the area of energy-efficient light production (solid-state lighting and full-color display), three primary colors (red, green, and blue) are highly essential[3][4]. To date, excellent red and green emissive materials are highly exploited over the blue counterpart[5][6]. First and foremost, the deep blue materials gain much attention over past decades because of their potential to increase color range of full-color OLEDs[7][8]. So far, performance of deep blue OLEDs is limited, which satisfy the standard of National Television System Committee, NTSC (Commission International de l'Eclairage (CIE) coordinates 0.14, 0.08) and European Broadcasting Union, EBU (CIE coordinate 0.15, 0.06). Therefore, for brilliant full-color display, blue emissive materials having CIEy value less than 0.1 are highly preferred[9][10]. Blue emitters have their own importance because they not only reduces the power consumption of the devices but also serve as host materials for phosphorescence via energy cascade to lower energy dopant, and increase color gamut in full-color display[11][12]. However, the fabrication of deep blue OLEDs is of great challenge due to its intrinsic wide energy band gap and unbalanced carrier/charge injection[13][14][15]. As we know that in the electroluminescence devices for the fluorescent emitters, internal quantum efficiency (IQE) is restricted up to 25%[16][17]. Phosphorescence emitters, generally Ir- and Pt- based complexes can harvest non emissive triplet excitons via intersystem crossing (heavy metal ion effect) to achieve IQE 100% by means of facial spin-orbit coupling, in spite of that, these materials lags behind in terms color purity (show sky blue) due to

large band gap also these materials use noble metal elements having a high cost which is undesirable for commercial application as well as deep-blue phosphorescent organic lightemitting diodes (PhOLEDs) suffers from certain degree of efficiency roll off[18][19]. From the last two decades, the vacuum deposition technique has been adopted for efficient OLEDs devices fabrication[20][21]. However, this technique is not cost-effective, inconvenient for flexible materials and large area display, and challenging for optimization of devices for future displays. To solve this issues, the first flexible OLED fabricated by Gustafsson *et al.* in 1992 based on solution processed technique.[22] This device fabrication technique is easy and economical for commercial application of OLEDs as well as can produce large area display with high performance because of uniform distribution of materials[23].

In this context, the fundamental understanding of design strategy of molecular materials and devices is highly required to achieve stable and high performance blue as well as white OLEDs. Phenanthroimidazole based emitters have been explored to construct efficient and stable blue emitters[24][25][26]. Recently, two emitters having phenanthroimidazole as acceptor and TPA as donor and N1 position of imidazole substituted with phenyl and cyano- phenyl group was designed and synthesized (structure are shown in Fig. S1). These fluorophores also showed deep blue emission in solution and the OLED device performance showed efficiencies of  $CE_{max}$  of 0.43 cd/A and 2.81 cd/A,  $PE_{max}$  of 0.93 lm/W and 2.05 lm/W, and  $EQE_{max}$  of 1.31% and 2.35% with blue CIE coordinate (0.18, 0.15) and (0.15, 0.14), respectively[27]. In 2017, two emitters (**MPPIS-TPA and MPPIS-Cz**) using phenanthroimidazole (electron-transporting moiety) as acceptor core and TPA/Carbazole (hole transporting moiety) as good donor were developed and the molecular structures are shown in Fig. S1. The OLED device based on these fluorophores shown efficiencies of  $CE_{max}$  of 1.46 cd/A and 1.52 cd/A,  $PE_{max}$  of 1.28 lm/W and 1.30 lm/W, and

 $EQE_{max}$  of 1.34% and 1.48%, with CIE coordinates of (0.15,0.12) and (0.16, 0.08) respectively[28].

Hence, here we report a two deep-blue emissive phenanthroimidazole (PI)-triphenylamine (TPA) (4-PIPTPA and 4-PIPCFTPA) based fluorophores. As PIs have thermally stable phenanthrene core and having five membered electron-deficient heterocyclic ring makes PI moiety as electron accepting group (A) and thus acting as electron-deficient group, will efficiently transfer the electrons in the devices. However, stable donor (D) triphenylamine (TPA) since it has potential to acts as efficient hole transporting ability, good thermal and morphological stabilities. Moreover, at the N1 position of the phenanthroimidazole here we substitute electron donating (Ph-CH<sub>3</sub>) and electron accepting (Ph-CF<sub>3</sub>) group to fine tune the excited state properties of the new emitters. As electron donating (-CH<sub>3</sub>) group helps to increase the  $\pi$ -conjugation strength as well as spectral efficacy and electron accepting ( $-CF_3$ ) group will increase the electron accepting capacity of imidazole moiety, hence improve the electron transporting properties and device efficiency of the fluorophores. The PI moiety when combined with effective hole transporting moiety i.e. TPA can effectively form bipolar materials[29]. In the present work, prior to the synthesis of the targeted fluorophores a quantum chemical analysis was performed in order to understand the electronic and optical characteristics of the targeted fluorophores. From the computational study it was observed that the targeted fluorophores show twisting confirmation, wide energy band gap ( $E_g > 3.28$  eV), having triplet energy of  $T_1 > 2.45$  eV, and separated HOMO-LUMO frontier molecular orbitals endows with bipolar nature of these fluorophores. Thus, obtained results from theoretical study inspire to synthesize these emitters. Herein, we report synthesis of the new fluorophores based on D- $\pi$ -A strategy and these structurally characterized by spectroscopic method. The optical, electrochemical and thermal properties of

these fluorophores studied systematically. The reported fluorophores show blue emissions with excellent quantum yields in solution and solid phase. To understand the HOMO-LUMO energy levels, for optimization of device structure electrochemical analysis has been carried out and same is compared with theoretical values. In addition, these new fluorophores were also used as blue-emitting dopants in solution-processed multilayer OLEDs, these two emitters exhibit blue emission and the doped device based on 4-PIPCFTPA shows good device performance than that of 4-PIPTPA: high external quantum efficiency (EQE<sub>max</sub>) of 2.9%, power efficiency (PE<sub>max</sub>) of 1.4 lm W<sup>-1</sup> and current efficiency (CE<sub>max</sub>) of 1.8 cd A<sup>-1</sup>.

### **Results and Discussions**

### **Theoretical calculations:**

To get further insight into the quantum chemical analysis, electronic structure at the molecular level, optimized geometries of the 4-PIPTPA and 4-PIPCFTPA were studied using density functional theory (DFT), calculation performed using B3LYP/6-31G (d, p) basic set[30]. Fig. 1 shows the optimized structure with dihedral angle between phenyl ring of donor and acceptor and spatial distribution frontier molecular orbitals of the new targeted fluorophores. The optimized structure of 4-PIPTPA and 4-PIPCFTPA shows twisted conformation, the twisted structure helps to reduces the  $\pi$ -conjugation, keeping the system emission into blue region[31]. Table.1 demonstrates the energy differences in the lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO) for 4-PIPTPA and 4-PIPCFTPA fluorophores. From the Fig. 1 the electron-density distribution points out that the HOMO of 4-PIPTPA and 4-PIPCFTPA were mainly localized on the electron rich triphenylamine (TPA) moiety and little contribution on phenyl spacer. The LUMOs of the 4-PIPTPA fluorophore were distributed over phenyl ring (between PI-TPA) to phenanthroimidazole moiety. Whereas, in case

of 4-PIPCFTPA fluorophore the LUMOs is localized mostly on imidazole-N1 substituted (Ph-CF<sub>3</sub>) moiety. The calculated HOMO-LUMO energy levels, energy band gaps (Eg), and first excited state energy levels of the targeted fluorophores are tabulated in Table 1. The estimated HOMO/LUMO energies of the synthesized fluorophores are -4.87/-1.25 eV (4-PIPTPA), and -4.96/-1.68 eV (4-PIPCFTPA), respectively. The estimated HOMO–LUMO energy gaps ( $E_g$ ) of 3.62 eV, and 3.28 eV for the fluorophores 4-PIPTPA, and 4-PIPCFTPA, respectively. Among these two fluorophores, the energy gap of the 4-PIPTPA is greater than that of 4-PIPCFTPA, due to separated HOMO-LUMO and distributed over donor (TPA) and acceptor (PI) respectively, which generate allowed electronic transitions [32]. The calculated HOMO-LUMO energy levels, energy band gaps (Eg), and first excited state energy levels of the targeted fluorophores are tabulated in Table 1. By carefully looking into the Frontier molecular orbitals (Fig S21), it is found that both the fluorophores show LE and CT features. In the case 4-PIPTPA there is a spatial separation of HOMO-LUMO with good molecular orbitals (MOs) overlap was observed with band gap of 3.62 eV and oscillator strength of 1.3466, hence we observed both locally excited (LE) and charge transfer (CT) states. However, in case of 4-PIPCFTPA due to electronwithdrawing group at N1 position of phenanthroimidazole results in pulling of electron density towards N1 substituted moiety (shows only CT), thus this full separation of HOMO and LUMO configuration leads to no overlap of the MOs involved with an less oscillatory strength, indicating the forbidden character of the transition between donor and acceptor. Whereas, the allowed singlet transition is found to be from HOMO to higher energy level LUMO+1 in the ground states as shown in Fig. S21 and respective transition are given Table S4.



**Fig. 1.** The optimized molecular geometries and spatial distribution of frontier molecular orbitals of the fluorophores.

The absorption spectra of the targeted fluorophores were theoretically calculated with the help of TD-DFT. The computed vertical transition, orbital contribution and oscillatory strength (f) of the targeted fluorophores tabulated in Table S4. Orbital distribution for each state is calculated. The calculated absorption spectra of these two emitters in gas phase are shown in Fig. 5c and in DCM phase are shown in Fig. S20 in SI. Atom coordinates of the fluorophores were given in the supplementary (SI8 in supplementary).

Fluorophores	НОМО	LUMO	HOMO-1	LUMO+1	$\mathbf{E}_{\mathbf{g}}$	S <sub>1</sub>	$T_1$	Oscillating
	(eV)	(eV)	(eV)	( <b>eV</b> )	(eV)	Gas/DCM	Gas/DCM	strength (f)
						(eV)	(eV)	
4-PIPTPA	-4.8671	-1.2501	-5.2692	-0.7224	3.62	3.15/3.06	2.43/2.45	1.3466
4-PIPCFTPA	-4.9672	-1.6838	-5.47001	-1.3894	3.28	2.99/3.04	2.45/2.47	0.1898

 Table 1. Calculated frontier molecular energy and excited states energy levels of the fluorophores.



Fig. 2. Chemical structures of the phenanthroimidazole derivatives.

**Experimental section.** 

Synthesis of *N*,*N*-diphenyl-4'-(1-(*p*-tolyl)-*1H*-phenanthro[9,10-*d*]imidazol-2-yl)-[1,1'biphenyl]-4-amine (4-PIPTPA)

A mixture of 4-PI-PT-Br (0.300 g 0.65 mmol), (4-(diphenylamino)phenyl)boronic acid (0.205g 0.71 mmol),  $Na_2CO_3$  (2.0 M aq. solution, 10 mL), toluene (20 mL), ethanol (10 mL), with  $Pd(PPh_3)4$  (0.037g 0.032 mmol) acting as catalyst was refluxed at 90 °C in an nitrogen

atmosphere for 24 h. The solution was cooled to room temperature, 30 mL water was added to the resulting solution and the mixture was extracted with dichloromethane (DCM). The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation. The residue was purified by column chromatography using the mixture of ethyl acetate/petroleum ether as the eluent to obtain the pure product as white solid. Yield: 75%, mp 244 °C, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 8.91 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 7.77(t, *J* = 7.6 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.2 Hz, 3H), 7.54-7.51 (m, 5H), 7.48-7.40 (m, 4H), 7.31 (dd, *J* = 14.8, 6.8 Hz, 6H), 7.15 (dd, *J* = 7.6, 2.4 Hz, 6H), 7.06 (t, *J* = 7.6 Hz, 2H), 2.57 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 150.82, 147.58, 140.63, 139.91, 137.41, 136.11, 133.96, 130.85, 129.72, 129.33, 129.22, 128.94, 128.81, 128.27, 128.25, 127.65, 127.29, 127.24, 126.27, 126.23, 125.57, 124.83, 124.51, 124.09, 123.76, 123.13, 123.07, 122.76, 120.93. IR (KBr, v/cm<sup>-1</sup>): 1589, 1518, 1495, 1471, 1450, 1383, 1291, 1147, 1004, 815, 746, 726, 693. MS (m/z): calcd for C<sub>46</sub>H<sub>33</sub>N<sub>3</sub>, 628.2747, found, 628.2757 [M + H].

Synthesis of *N*,*N*-diphenyl-4'-(1-(4-(trifluoromethyl)phenyl)-*IH*-phenanthro[9,10*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-amine (4-PIPCFTPA): The synthetic procedure of 4-PIPCFTPA was same as that of compound 4-PIPTPA by replacing 4-PI-PT-Br with 4-PI-PCF3-Br. Yield: 77%, mp 244 °C, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 8.90 (d, *J* = 7.2 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.72 (dd, *J* = 14.8, 8.8 Hz, 3H), 7.58-7.48 (m, 6H), 7.35-7.27 (m, 7 H), 7.15 (dd, *J* = 7.4, 1.2 Hz, 6H), 7.06 (t, *J* = 7.2 Hz, 2H). <sup>13</sup>C{<sup>19</sup>F}-NMR (100 MHz, CDCl<sub>3</sub>, TMS,  $\delta$  ppm) : 147.71, 147.52, 141.13, 137.83, 133.60, 129.37, 129.34, 128.34, 128.31, 127.67, 127.54, 127.36, 127.32, 127.05, 126.49, 126.42, 125.90, 125.15, 124.56, 124.36, 123.68, 123.14, 122.84, 122.67, 120.58. IR (KBr, v/cm<sup>-1</sup>): 1592, 1522, 1495, 1475, 1324, 1294, 1167, 1120, 1067, 858, 756, 728, 693. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>, TMS,  $\delta$  ppm): -62.40 (s). MS (m/z): calcd for C<sub>46</sub>H<sub>30</sub>F<sub>3</sub>N<sub>3</sub>, 682.2465, found, 682.2466 [M + H].



Scheme 1. Synthesis routes for the phenanthroimidazole derivatives.

### **Thermal properties:**

The thermal stabilities of the new fluorophores were investigated using thermal gravimetric analysis (TGA) in the presence  $N_2$  atmosphere. TGA analysis been conducted from ambient temperature to 800°C (10 °C/min) and TGA curves of phenanthroimidazole derivatives were shown in Fig. 3 and respective data summarized in Table 2. The thermograms shows that the thermal decomposition temperature (T<sub>d</sub>) defined by the weight loss corresponding to 5 % were measured to be 446°C and 422°C for 4-PIPTPA and 4-PIPCFTPA, respectively. Both fluorophores show excellent thermal stability benefited from the rigid molecular structure of phenanthroimidazole unit and also suggest that the morphology of the fluorophores does not changed at high temperature as heat generates during operation of OLEDs devices[33]. The

results propose that presently explored fluorophores highlighting excellent high decomposition temperature and it is the fundamental prerequisites for OLEDs since high  $T_d$  enhances the lifetime of the devices.



Fig. 3. TGA curves of phenanthroimidazole derivatives.

### **Optical properties:**

The absorption and photoluminescence (PL) study of the synthesized fluorophores were carried out in the solution (Toluene ( $10^{-5}$  M)) and in the solid phase. Detailed photophysical data of new born fluorophores were listed in Table 1. From the UV-vis spectra of fluorophores in solution (Fig. 4 a), shows the same absorption pattern due to identical structural backbone and shows two strong absorption band. The strong absorption bands in the lower wavelength at around ~294 nm small shoulder ~309 nm for both the fluorophores which is attributed to the  $\pi$ - $\pi$ \* transition originates from aromatic ring attached to N-atom in imidazole ring[34]. However, the absorption band in the lower energy at ~365 and 364 nm for 4-PIPTPA and 4-PIPCFTP, respectively observed due to the presence of intramolecular charge transfer from donor (TPA) to acceptor

(PI)[35]. The solid states UV-vis absorption spectra Fig. 4b, also recorded for the fluorophores and found strong absorption band at 351 and 370 nm for 4-PIPTPA and 4-PIPCFTPA, respectively and small red shift shows existence of intermolecular  $\pi$ - $\pi$ \* stacking in the solid states[36].



**Fig. 4.** UV-vis absorption spectra of the fluorophores in Toluene solution a) and solid b). In Fig. 5a, the substituents present on the N1 position of the imidazole influence the PL emission spectra of the fluorophores i.e. the PL peaking wavelength 417 nm were observed for 4-PIPTPA and 422 nm observed for 4-PIPCFTPA with shoulder peaks at 437 nm and 440 nm for 4-PIPTPA and 4-PIPCFTPA, respectively indicates substitution of electron withdrawing moiety at N1 position of imidazole shows red shift emission wavelength than elctron donating. The shoulder peaks in Toluene is observed due to localy excited states is predominent in low polar solvent. In addition, the obvious red-shift in the PL spectra from solvent to solid (Fig.5b), suggest an occurrence of strong intramolecular aggregation in the synthesized fluorophores[37][38]. Additionally, the PL spectra of both the fluorophores show a shoulder peak at 451 nm and 466 nm for 4-PIPTPA and 4-PIPCFTPA respectively; these may be observed due to the excimer formation in the solid states. Fig.5d shows the CIE color coordinates of new born deep-blue

emissive materials obtained from the PL emission and corresponding x and y color coordinates are tabulated in Table S3. Among these two fluorophores, 4-PIPTPA emitter exhibited deepblue CIE coordinates in solution as well as solid (0.151, 0.060) and (0.156, 0.104). The absolute quantum yield ( $\Phi$ ) of the deep-blue fluorophores were measured in solution as well as in solid phase and the digital images of fluorophores are shown in Fig. S18 and Fig. S19.



**Fig. 5.** PL spectra of the fluorophores in solution a), solid b), c) Simulated UV-vis absorption spectra of phenanthroimidazole derivatives in gas phase obtained from TD-DFT, and d) The CIE

chromaticity diagram phenanthroimidazole derivatives in solutions and solid phase. Both the synthesized fluorophores exhibit good quantum yield in solution and solid, which is beneficial for blue OLEDs. The measured QY (solution/solid) listed in Table 2, and found to be

4-PIPTPA (63.9% /32.3%) and 4-PIPCFTPA (76.3%/84.9%), respectively. The observed higher QY for the fluorophores due to high rigid geometry increased the proportion of radiative transition because of molecular interactions. The lover PLQY of 4-PIPTPA in solid states may be observed due to the exciplex formation or  $\pi$ - $\pi$  stacking interaction is more in case of *p*-tolyl substituted fluorophores than p-CF3, which may increases the vibrational non-radiative transition in the solid states [3]. To further get insight into the excited states properties of these two deepblue emmisive materials, the decay analysis were studied by using time-correlated single photon counting (TCSPC) technique under the excitation by suitable laser source and the dacays of the lifetime are shown in Fig. 6 and corresponding life time data were given in Table 2. The lifetime of all the synthesized fluorophore were calculated by using equation (1)

$$(\tau) = I_0 + A_1 \exp(-\frac{t}{\tau}) \tag{1}$$

Where,  $I_0$  is the offset value ( $I_0 = 0$ ),  $A_1$  is the scalar quantity acquired from the curve fitting, t is the time in ns and  $\tau$  is the exponential decay time. The decay analysis also been carried out for these two deep-blue emissive materials doped in CBP host and the results are shown in Fig S17. The fluorophore shows higher lifetime when doped with 1 wt% in CBP as compared with its undoped state. 4-PIPTPA and 4-PIPCFTPA shows lifetime of 2.40 and 3.23 ns when undoped as compared to 3.43 and 3.73 ns in doped phase, respectively. The expected reason behind may be due to the favorable host-guest energy transfer in the emissive layer compared to counterpart undoped devices[39] [40][41].



Fig. 6. PL Lifetime decay curves of phenanthroimidazole derivatives in solution.

Compoun	T <sub>d</sub> <sup>a</sup> ℃	Solution		Solid		Absolute quantum yield (Φ)		Lifeti me
ds		Abs (nm)	PL	Abs	PL (nm)	Solution	Solid (%)	(η ) ns
			(nm)	(nm)		(%)		
4-PIPTPA	446	293, 309,	417, 437	351	434, 451	63.9	32.3	2.40
		365						
4-	422	294, 309,	422, 440	370	450, 466	78.3	84.9	3.23
PIPCFTP		364,						
Α								
<sup>a</sup> Temperature corresponding to 5% weight loss								

**Table 2.** Key photophysical properties of phenanthroimidazole derivatives

### Cyclic voltammetry study.

To know electrochemical properties of the new born fluorophores, the cyclic voltammetry (CV) were carried out in anhydrous DMF solution  $(10^{-5} \text{ M})$  and  $Bu_4NClO_4$  (0.1 M) used as a supporting electrolyte at 298±1 K. The Fig. 7 shows the cyclic voltammograms of the synthesized fluorophores and resultant electrochemical data were summarized in Table 3. These

two fluorophores possess quasi-reversible redox behaviors, which strongly indicate that the fluorophores possess "bipolar" properties. The onset oxidation potential ( $E_{oxd}^{onset}$ ) found to be 1.37 and 1.32 V vs. Ag/AgCl for 4-PIPTPA and 4-PIPCFTPA, respectively and onset reduction potential ( $E_{red}^{onset}$ ) occurs at -1.21 and -1.63 V vs. Ag/AgCl for 4-PIPTPA and 4-PIPCFTPA, respectively. The HOMO and the LUMO energy levels of the deep-blue fluorophores can be calculated by using the equation (2) and (3) reported by de Leeuw *et. al.*[42].

$$E_{HOMO} = -(E_{ox}^{onset} + 4.4) \quad eV$$
<sup>(2)</sup>

$$E_{LUMO} = -(E_{red}^{onset} + 4.4) \quad eV$$
(3)

The HOMO/LUMO energy levels of the fluorophores are -5.77/-3.19 eV (4-PIPTPA), and - 5.72/-2.77 eV (4-PIPCFTPA) with energy band gap of 2.58 eV (4-PIPTPA), and 2.95 eV (4-PIPCFTP).



Fig. 7. Cyclic voltamogram of phenanthroimidazole derivatives.

Compounds	E <sup>onset</sup> <sub>red</sub> (V)	$E_{oxd}^{onset}$ (V)	HOMO (eV)	LUMO (eV)	Energy gap	
					(eV)	
4-PIPTPA	-1.21	1.37	-5.77	-3.19	2.58	
4-PIPCFTPA	-1.63	1.32	-5.72	-2.77	2.95	

**Table 3.** Electrochemical properties of phenanthroimidazole derivatives.

### **Electroluminescence properties:**

Blue emitters based on imidazole having TPA unit have shown considerable interest, which helps to improve their optical and charge transfer properties with better functional fluorophores. To evaluate the electroluminescence (EL) properties of the novel deep-blue emitters, i.e. 4-PIPTPA and **4-PIPCFTPA** initially, undoped devices with structure ITO/PEDOT:PSS/emitters/TPBi /LiF/Al are fabricated by incorporating newly synthesized dyes as emitting layer. Since the undoped devices displayed poor EL properties due to thin-film stability, the doped devices are fabricated utilizing 4-PIPTPA and 4-PIPCFTPA as emitter with device structure ITO/PEDOT:PSS/CBP: new emitters/TPBi/LiF/Al to reduce aggregation of emitters and enhance the thin-film stability and thereby enhancement in EL properties of doped devices as comparing with undoped devices. Fig. 8 (a) exhibits the energy-level diagrams of fabricated deep blue OLEDs with different newly synthesized emitters. Fig. 8 (b) displays the energy-level diagrams with doped emitters into CBP based OLED devices.



**Fig. 8.** Energy-level diagrams of the studied devices with (a) undoped and (b) doped emitters. Among these two newly synthesized deep blue emitters, 4-PIPCFTPA demonstrates the high performance as comparing with 4-PIPTPA emitter. The EL characteristics curves such as luminance-voltage, current-density-voltage, power-efficacy-luminance, current-efficacy-luminance, and EL spectra for emitter 4-PIPTPA and 4-PIPCFTPA are shown in Fig. 9 and 10, respectively. The EL characteristics of these emitters-based deep blue OLED devices are summarized in Table 4.

The synthesized fluorescence blue-emitter materials were used as a neat emitter film (100%) as in the case host CBP among different concentrations of the synthesized blue emitters mainly 1, 3 and 5% for emissive layer. For the doped devices, the different concentrations (1,3 and 5 wt%) of emitters are doped in the CBP host. It can be seen from the energy-level diagram that the CBP exhibits good alignment with newly synthesized emitters, which leads to facilitate perfect hostto-guest energy transfer and the thin-film uniformity. From Table 4 and Fig. 9 (a-b) and Fig. 10 (a-b) show the increment in the luminance and current-density as voltage increases, which indicates that the devices exhibit the perfect characteristics of a diode and possess low turn-on voltage for 1wt% concentration as comparing with 3 and 5wt%. As the concentrations of dopants increases from the 1 to 5wt%, the luminance and current density increases, which demonstrates that the mobility of emissive layer is greatly influenced by the dopant concentration and induces the charge imbalance in emissive layer.



**Fig. 9.** 4-PIPTPA doping concentration effects on properties such as (a) luminance-voltage, (b) Current-density-voltage, (c) power-efficacy-luminance, (d) current-efficacy-luminance, (e) luminance-current-density, and (f) EL spectra using the CBP host with 1, 3, and 5 wt% dopant concentrations.

Table 4. Doping concentration influences on electroluminescent properties such as power
efficacy (PE), current efficacy (CE), external quantum efficiency (EQE), CIE coordinates, and
maximum luminance (L <sub>max</sub> ) of 4-PIPTPA and 4-PIPCFTPA.

Dopants	Guest Conc. (%)	$\frac{PE_{100} / CE_{100} / EQE_{100}}{(Im W^{-1} / cd A^{-1} / 9\%)}$	$\frac{PE_{1000}^{-1}/CE_{1000}^{-1}}{EQE_{1000}^{-1}}$ (Im W <sup>-1</sup> /cd A <sup>-1</sup> /	PEKCE/ EQE (Im W <sup>-1</sup> / cd A <sup>-1</sup> / %)	CIE	L <sub>max</sub> (cd/m <sup>2</sup> )
4-PIPTPA	1	0.2/0.4/1.4	-/-/-	0.4/0.5/1.6	(0.17, 0.09)/-	653
	3	0.6/1.0/1.0	0.2/0.4/0.6	0.6/1.0/1.0	(0.17, 0.14)/-	1054
	5	0.4/0.8/0.8	0.2/0.6/0.8	0.4/0.8/0.8	(0.17, 0.13)/- (0.17, 0.12)	1531
	100	0.2/0.2/0.1	-/-/-	0.2/0.2/0.1	(0.24, 0.41)/ -	683
4- PIPCFTPA	1	0.3/0.5/2.2	-/-/-	0.4/0.6/2.7	(0.17, 0.07)/ -	543
	3	0.8/1.2/2.6	0.2/0.4/2.4	1.4/1.8/2.9	(0.18, 0.12)/ -	1034
	5	1.0/1.7/1.5	0.4/0.9/1.2	1.3/1.9/1.5	(0.20, 0.18)/ -(0.18, 0.13)	1583
	100	0.4/0.6/0.2	0.3/0.6/0.2	0.4/0.6/0.2	(0.32, 0.56)/- (0.32, 0.55)	2109



**Fig. 10.** 4-PIPCFTPA doping concentration effects on properties such as (a) luminance-voltage, (b) Current-density-voltage, (c) power-efficacy-luminance, (d) current-efficacy-luminance, (e) luminance-current-density, and (f) EL spectra using the CBP host with 1, 3, and 5 wt% dopant concentrations.

Fig. 9 (c-d) demonstrates that the 4-PIPTPA exhibits maximum power efficacy (PE) of 0.4 lm/W and current efficacy (CE) of 0.5 cd/A at 1wt% doping concentration of 4-PIPTPA dopant into CBP host. Fig. 10 (c-d) exhibits the 3wt% 4-PIPCFTPA emitter-based OLED possess a maximum PE of 1.4 lm/W, EQE of 2.9% and CE of 1.8 cd/A. The performance of 4-PIPTPA based OLED decreases as the concentration of dopants increases from 1 to 5wt%, which is attributed to the insufficient energy transfer between host and dopant as on increasing the concentration of dopant, more dopant moieties are present in the emissive layer, which in turn may lead to charge trapping of host and charge deficiency. We also observed similar pattern for another emitter in Fig. 10. Fig 9 (e) and 10 (e) demonstrates the luminance increases as current-density increases attributing to the more efficient recombination caused by high mobility carriers into emissive layer. Furthermore, it is also observed that the increasing doping concentration enhancing the luminance in the devices, which is attributed to exciton quenching. Fig. 9 (f) and Fig. 10 (f) demonstrates the EL spectra of the studied devices and indicates that the concentration

influences the EL emission peaks. As the concentration increases from 1-5 wt%, the red shifting of EL spectra is observed at 5 wt%, indicative of host charge trapping and a slight decrement of CBP emission from 390-440 nm sufficiently suggest the inadequate energy transfer between host and dopant[43][44]. As a result, the device containing the 4-PIPCFTPA deep blue emitter with host CBP showed superior EL performance as comparing with other devices containing different emitter materials doped into CBP. Additionally, we investigated the charge carrier properties of the novel synthesized emitter materials by fabricating the single carrier devices, i.e., hole-only (HOD) and electron-only (EOD) devices. The HOD device structures, we fabricated as follows: ITO/PEDOT: PSS (35 nm)/TAPC (30 nm)/ 4-PIPTPA or 4-PIPCFTPA (20 nm)/TAPC (30 nm)/Al (100 nm), although, for EOD devices we use the structure as ITO/TPBi (35 nm)/ 4-PIMCFTPA or 4-BICFTPA (20 nm)/TPBi (35nm)/LiF (1 nm)/ Al (100 nm). The energy level diagrams of the HOD and EOD device structures are illustrated in Fig, 11 (a) and (b), respectively. The TAPC and TPBi layers were used to prevent electron and hole injection from cathode and anode. The current density-voltage characteristics of the HOD and EOD devices are illustrated in Fig. 11(c) and (d), respectively. The hole current density of HOD is higher than that of the electron current density of EOD, which endorse that both emitters are p-type materials. The 4-PIPCFTPA based HOD device shows higher hole current-density than 4-PIPTPA based HOD device, which established higher hole mobility of 4-PIPCFTPA than 4-PIPTPA Fig. 11(c). Furthermore, here also found that, at higher voltage, the electron current-density of 4-PIPTPA based EOD device is slightly higher than that of 4-PIPCFTPA based EOD device, Fig. 11(d), which shows somewhat higher electron mobility of 4-PIPTPA than 4-PIPCFTPA.



**Fig. 11.** (a) and (b) illustrate the energy-level diagrams of the hole-only and electron-only devices, respectively as well as (c) and (d) show their respective hole and electron current density characteristics.

### **Conclusion:**

In summary, two novel deep-blue emitting donor- $\pi$ -acceptor (D- $\pi$ -A) fluorophores were successfully designed and synthesized by connecting hole transporting triphenylamine (D) and electron transporting phenanthroimidazole (A) moiety with electron donating (Ph-CH<sub>3</sub>) and electron accepting group (Ph-*p*-CF<sub>3</sub>) substitution at the N1 position of each imidazole by using cost effective and easy solution processed method. These fluorophores showed deep blue emission with good quantum yield in solid and solution state as well as good thermal stability. Moreover, these fluorophores were used as dopant materials and undoped, doped devices were fabricated. Furthermore, the undoped devices showed deep blue electroluminescence with high

current density and low brightness compared with the doped devices. The doped OLED devices based on 4-PIPCFTPA fluorophores as dopants showed deep blue emissions and exhibits high efficiencies,  $PE_{max}$  of 1.4 lm/W,  $CE_{max}$  of 1.8 cd/A, and  $EQE_{max}$  of 2.9 %, with CIE coordinates of (0.18, 0.12) at 3 wt% doping concentration and  $PE_{max}$  of 0.4 lm/W,  $CE_{max}$  of 0.6 cd/A, and  $EQE_{max}$  of 2.7 %, with CIE coordinates of (0.17, 0.07) at 1 wt% doping concentration. These results are in close proximity to the standard deep-blue emission coordinates (0.14, 0.08) as prescribed by the NTSC as y value of these emitters is lower than standard value.

### **Supporting Information:**

Supporting information includes of general information about characterization, synthesis of intermidiates, NMR spectra (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR), and Mass spectra of the compounds. As well as the CIE coordinates, Quantum yield studies for the compounds in solutions and solid phase, the calculated UV-vis absorption spectra and vertical transition composition and atom coordinates of all the fluorophores.

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### Highlights.

- Two highly twisted deep-blue emitters based on triphenylamine and • phenanthroimidazole (D- $\pi$ -A) moieties were designed and synthesized.
- The synthesized emitters showed high thermal stability and good photoluminescence quantum yields.
- HOMO and LUMO separation indicates fluorophores having good carrier ٠ transporting properties.
- Solution processed doped OLED device based on 4-PIPCFTPA shown deep-blue • electroluminescence (0.17, 0.07) close to NTSC standard with EQE<sub>max</sub> of 2.7%.

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The authors declare that there is no conflicts of interest

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