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# Efficient near ultraviolet emissive (CIEy < 0.06) Organic Light-Emitting Diodes based on Phenanthroimidazole-Alkyl spacer-Carbazole fluorophores: Experimental and Theoretical investigation

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## Abstract:

Efficient near ultraviolet light-emitting materials are of particular importance in organic light emitting devices (OLEDs) because of its impending application in high-quality flat panel displays and white OLEDs. In the present investigation, a series of efficient Near-UV light emitting fluorophores based on Donor-spacer-Acceptor (D-s-A) geometry were design and synthesized. In this design strategy, we have linked carbazole group with phenanthroimidazole unite through alkyl spacer (capable of hole and electron transporting in the device) with different functional groups at the N1 position of imidazole moiety. All the fluorophores were structurally established by spectroscopic techniques and the synthesized fluorophores are shown near-UV emission in dichloromethane (DCM) and it indicates that the N1 substitutions of imidazole moiety are played an imperative role in the photophysical properties of the synthesized fluorophores. Cyclic voltammetry investigation revealed that the fluorophores have low-lying energy levels of the LUMO ranging from -2.88 eV to -3.35 eV, and energy of the HOMO ranging from -5.55 eV to -5.80 eV, suggesting that they may possess good charge-transporting properties. The theoretical calculation experiment has been executed to verify the excited state properties of newly synthesized fluorophores and indicates that these twisting D-spacer-A fluorophores exhibit high triplet excited state (ranging from 2.70 to 3.12 eV). The resultant OLED devices based on these fluorophores exhibited near UV-emission with Commission International de L'Eclairage (CIE) color coordinates of y < 0.05 (close to NTSC standard value) and maxima of EL spectra centered in between 395-405 nm at a particle doping concentration. The device using the PIFOCz emitter possesses a favourable maximum external quantum efficiency (EQE) of 3.3%.

**Keywords:** Carbazole, Phenanthroimidazole, Fluorophores, DFT computations, near UV OLEDs.

### Introduction:

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In the past two decades, owing to their potential application in large size flat panel displays (including flexible displays) and solid state lighting sources, the development of deep blue to near UV organic light emitting diode materials has attracted much attention.<sup>1-3</sup> In addition, these fluorophores gained additional importance, due to their low power consumption and their ability to increase the color range of full-color organic light emitting diode (White OLED)<sup>4,5</sup> and also be useful as hosts (targeting to surpass the aggregation- or concentration-induced luminescence quenching in fluorescent as well as triplet emitter) to generate other primary color (red and green) OLEDs.<sup>6-11</sup> It is also worth to note that achieving high performance in the device with the near UV emitters are still bottle neck and the external quantum efficiency (EQE) achieved so far is typically < 2%, this restriction is attributed to the intrinsic wide band-gap that induces the unbalanced charge injection/transport in the device. White OLED displays require the emission of red, green and blue (RGB) light (primary colors). The development of highly efficient primary color emitters is one of the most important tasks for making OLEDs into commercial products.<sup>12-14</sup> In the National System Committee (NTSC) color system, which uses Commission Internationale del'Eclairage (CIE) coordinates as a key parameter, for the deep blue materials CIE coordinates of (0.14, 0.08)are required, the CIEy is further improved to 0.06 by the European Broadcasting Union (EBU).<sup>15-18</sup> Recently, rapid improvement occurs in the efficiencies of OLED, efficient fluorescent and phosphorescent materials have already emerged.<sup>19-25</sup> However, there are still some vital problems that is inevitable (i.e. wide energy band gap) in the development of highly efficient deep-blue materials with good color purity. Unbalanced charge injection as well as transporting is a foremost problem in deep-blue OLEDs.<sup>26-28</sup> Recently, phenanthroimidazole (PI) has appeared as a building block for the synthesis of highly-efficient blue luminescent materials with simple synthesis

procedure, good thermal stability properties, satisfactory color purity, high fluorescent quantum yield.<sup>29-37</sup> After various theoretical and experimental investigation, C2 and N1 in the heterocyclic imidazole ring were identified as a two important substitution position, and the structure-property relationships were used as active direction for deep blue PI-based materials with good performance.<sup>38-42</sup> The carbazole is a widely used functional group in the construction of efficient luminescent materials for OLED application.<sup>43-47</sup> Carbazole has better hole transporting as well as injection capability, due to the electron donating character of carbazole and it is commonly linked with electron deficient moieties in various ways to construct bipolar emitters. Carbazole 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP) 1.3-Bis(Nderivatives. such and as carbazolyl)benzene (mCP) are most widely used host for triplet emitters based phosphorescent OLEDs because these materials have sufficient large triplet T<sub>1</sub> energy.<sup>48</sup>

In 2013, Yuguang Ma and co-workers<sup>49</sup> reported two blue emitting conjugated fluorophores (M1and M2, structures are shown in Fig. S1 in SI) with carbazole and phenanthroimidazole as D and A subunits, respectively. OLED based on these emitters showed deep blue EL emission with  $\lambda_{EL}$  of 420 nm (M1) and 428 nm (M2) and EQE of 1.94 % and 3.02 %, respectively. Recently, R. Butkute, *et al.* published blue emitting conjugated fluorophores<sup>50</sup> (7, 8, 9 and 10, structures are shown in Fig. S1 in SI) with phenanthroimidazole and carbazole, triphenylamine as the A and D functional black, respectively. The fabricated non-doped OLED devices showed blue emission with EQE of ~1 %. By using 10-blue emitter the white OLED device also fabricated and the white OLED device showed white EL emission with the EQE of 2.9 %.

A bipolar molecule can be prepared by chemical connectivity between hole- and electron-transport moieties with (conjugated or non-conjugated) and without spacer group. In which a spacer group will be conjugated aromatic group (phenyl or biphenyl or styrene)<sup>51-55</sup> or non-conjugated aliphatic

group (single bond or an alkyl chain).<sup>56-58</sup> Till date numerous conjugated bipolar materials have been developed for White OLEDs, <sup>51-54</sup> few non-conjugated bipolar materials have been reported. <sup>56-</sup> <sup>58</sup> Non-conjugated and conjugated bipolar materials without flexible linkage tend to be bulky and rigid, thus limiting the solubility and the ability to form morphologically stable films. The discussed design strategy context, we report non-conjugated fluorophores containing the aliphatic linkage between the two charge transport moieties (hole-/electron- transporting). We have synthesized a series of PI derivatives (Fig. 1.) by taking thermally stable phenanthroimidazole as electron-transporting moiety and carbazole as hole-transporting moiety with the different functional groups at the N1 position of the imidazole ring.<sup>59</sup> All the fluorophores were structurally confirmed by spectroscopic technique. The synthesized fluorophores are shown deep blue photoluminescence (PL) emission in dichloromethane solution. Cyclic voltammetry investigation revealed that these fluorophores show bipolar charge transporting properties. The theoretical calculation also was performed to now the electronic structure of the fluorophores and it indicates that these twisting D-s-A fluorophores exhibit high triplet excited state. The doped OLED device based on PIFOCz radiates near UV-emission (CIEx, y = 0.17, 0.05) with a forward viewing maximum EQE of 3.3%.



Fig. 1. Chemical structure of PI derivatives.

#### **Results and Discussion**

#### Synthesis and Characterization:

The synthetic route of the target PI derivatives is shown in Scheme 1. The Fl-NH<sub>2</sub>, 4-(4-bromobutoxy) benzaldehyde (Intermediate-1) and 4-(4-(9H-carbazol-9-yl)butoxy) benzaldehyde (Intermediate-2) were synthesized according to a modified literature procedure.<sup>60, 61</sup> The target PI derivatives were synthesized by a condensation reaction between phenanthrene-9,10-dione, amine derivatives, and Intermediate-2 in the presence of ammonium acetate and acetic acid. The synthesized fluorophores were structurally characterized by Nuclear Magnetic Resonance Spectroscopy, Mass Spectrometry, and Infrared Spectroscopy.



PIPOCz PIPTOCz PITBOCz PIFOCz Scheme 1. Synthetic routes of PI derivatives.

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Thermal properties:
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The thermal properties of PI derivatives were investigated by thermogravimetric analysis (TGA) from 0 to 800 °C at a heating rate of 10 °C/min under a N<sub>2</sub> atmosphere. As shown in Fig. 2, all the fluorophores showed almost similar decomposition progress starting from the same structural framework. TGA curves reveal that the major degradation temperature (T<sub>d</sub>) of 5% weight loss of PI derivatives is 326 °C (PIPOCz), 335 °C (PIPTOCz), 275 °C (PITBOCz), and 375 °C (PIFOCz), respectively (Table 1), which could be attributed to the decomposition of fluorophores fragments (N1 subunits) present in the fluorophores and final decomposition undergoes at 544 °C (PIPOCz), 573 °C (PIPTOCz), 536 °C (PITBOCz), and 525 °C (PIFOCz), respectively, which could be attributed to fragments of alkyl spacer, carbazole and phenanthroimidazole groups present in the fluorophores. Among all the fluorophores, PIFOCz fluorophore showed slightly more degradation temperature (5% weight loss), it is due to increased molecular mass with the addition of thermally stable fluorene moiety connected at N1 position of the imidazole ring. When the molecular weight increases the thermal decomposition temperature (T<sub>d</sub>) also increases. <sup>37, 62</sup> These results indicate that synthesized PI derivatives provide desirable thermal properties, which are favourable for use these fluorophores in OLED device.



Fig. 2. Thermogravimetric curves of PI derivatives.

#### **Photophysical properties:**

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The photophysical properties of the PI derivatives were investigated by UV-vis and PL spectrometry. The absorption and PL emission spectra of the fluorophores are shown in Fig. 3 and corresponding data is tabulated in Table 1. All the fluorophores exhibit similar spectral behaviour (in solution Fig. 3a) with three major absorption bands. The absorption bands around 260 nm can be assigned to the  $\pi$ - $\pi$ \* transition of the phenyl moiety.<sup>63</sup> The bands at 294 nm were attributed to the  $\pi$ - $\pi$ \* transition of the carbazole moieties in all the synthesized fluorophores.<sup>64</sup> The observed higher-wavelength weak absorption bands 360 nm probably originate from the  $\pi$ - $\pi$  interaction of the fluorophores. The absorption of spectra of fluorophores in solid was found to be broad and red-shifted (10 nm) due to  $\pi$ - $\pi$  packing interactions (Fig. 3c.).<sup>64</sup> The optical band gap of the fluorophores was calculated by converting solid absorption data into the Kubelka-Munk

function.<sup>65</sup> The obtain spectra is shown in Fig. 3b the found band-gaps are well matching with the experimental analysis data (CV measurement).

The PL emission spectra of fluorophores (Fig. 3a and 3d) exhibited deep-blue emission with peak wavelength at ~400 nm in DCM solution, while the PL emission of the fluorophores is red-shifted in the solid because of the intramolecular  $\pi$ - $\pi$  packing interaction.<sup>66</sup> The CIE chromaticity coordinate image of the fluorophores in solution and solid were shown in Fig. S19 in SI and corresponding data is summarised in Table S2. The flurescence measurement also been executed in different polar and non-polar solvents for PIPOCz fluorophor (Fig. S20 in SI) and the fluorophore showed the similar emission spectra (not much red-shift is obsorbed), indicating that no strong intramolecular charge transfer (ICT) existed in PIPOCz fluorophor. The quantum yield (PLQY) of the fluorophores was calculated in solution and solid by using an integrating sphere. The quantum yield of the fluorophores was calculated by using equation (S1).<sup>67</sup> The calculated quantum yield results are listed in Table 1. The measured quantum yield digital images are shown in the SI6 section in the SI. PLQYs in DCM solution was estimated to be 26.1, 24.6, 22.4, and 25.2 % for PIPOCz, PIPTOCz, PITBOCz, and PIFOCz. Whereas in the solid state, PLQY is increased as 54.9, 38.7, 37.4, and 47.27 %, respectively, it is due to that intramolecular  $\pi$ - $\pi$  packing interaction in sold phase of synthesized molecules. The high solid-state PLQY values of these fluorophores benefit from the twisted molecular conformation and suggest their potential to work as the emitting layer in OLEDs.



Fig. 3. a) UV absorption and PL emission spectra of fluorophores in DCM solution, b) optical bandgap of the fluorophores, c) UV absorption spectra of fluorophores in the solid state, and d) PL emission spectra of fluorophores in the solid state.

Fluorophores	Tda	Solution		Solid		Absolute quantum yield (Φ)	
	(°C)	Abs (nm)	PL	Abs	PL	Solution	Solid
			(nm)	(nm)	(nm)	(%)	(%)
PIPOCz	326	248, 294, 315, 363	405	365	413, 434,	26.1	54.9
					476, 507		
PIPTOCz	335	248, 294, 315, 362	405	290,	411, 505	24.6	38.7
				375			
PITBOCz	275	260, 294, 315, 362	402	375	408, 433,	22.4	37.4
					457, 490		
PIFOCz	375	260, 294, 364	401	310,	400, 420,	25.2	47.27
				370	446, 475		
<sup>a</sup> Thermal decomposition temperature corresponding to 5% weight loss							

Table 1. Key photophysical properties of PI derivatives

#### **Theoretical calculations:**

Further insight into the molecular orbital distributions of the PI derivatives was gained by Density Functional Theory (DFT) calculation, which was carried out at the level of B3LYP/6-31(d) basis set to the investigative ground state and excited state energy level of the PI derivatives.<sup>68</sup> The optimized geometries and calculated HOMO/LUMO energy levels of PI derivatives are shown in Fig. 4 and 5 and Table 2 shows the calculated results of all fluorophores. Fig. 5 shows small energy differences in the highest occupied molecular orbitals (HOMO) of all the PI derivatives which are mostly distributed on the phenanthroimidazole moiety. However, unlike the case of HOMOs, all the PI derivatives have shown a great energy difference in the lowest unoccupied molecular orbitals (LUMOs). For PIPOCz, PIPTOCz and PITBOCz fluorophores the LUMO is distributed from phenanthroimidazole moiety to N1 substitution group, whereas in PIFOCz fluorophore mostly on the N1 substitution groups (Fig. 5). The almost complete separation of HOMO and LUMO energy levels (PIFOCz) suggests that the separation of electron cloud of HOMO and LUMO could afford the transporting channels between hole and electron, which may endow the fluorophore with the ability of bipolar charge transport in the device. In addition, the excited energy levels (singlet and triplet) of synthesized fluorophores were also been calculated by using Time-Dependent-DFT (TD-DFT)/B3LYP method. The calculated singlet and triplet energy values are tabulated in Table 2. The obtained triplet energy of the synthesized fluorophores ranging from 2.70 to 3.12 eV (in gas phase). The obtained triplet energy values of non-conjugated fluorophores are higher than that of conjugated 7, 8, 9 and 10 fluorophores (ranging from 2.39 to 2.65 eV in gas phase),<sup>50</sup> because the conjugated molecules have finite  $\pi$ -conjugation between D and A subunits.<sup>69</sup> These results reveal that separation of D and A subunits with non-conjugated alkyl spacer, consequently arrest communication between D and A subunits and boost the triplet energy levels. By using the optimized geometry of ground-state, the absorption spectra of the synthesized fluorophores were calculated with the help of TD-DFT. The related absorption wavelength (nm), oscillator strength, major configuration, and their assignment are collected in the SI7 section. Orbital compositions of each excited state have also been calculated. These results give complete information about the absorption spectra. Simulated absorption spectra of PI derivatives are shown in Fig. S25 in SI and their corresponding data are given in the SI7 section. In addition, atomic coordinates of PI derivatives were given in the SI9 section.



Fig. 4. Optimized structures of all the fluorophores

**Table 2.** Calculated Frontier Molecular Energy Levels of fluorophores.

Fluorophores	НОМО	LUMO	$\mathbf{E}_{\mathbf{g}}$	S <sub>1</sub> (gas)	T <sub>1</sub> (gas)	S <sub>1</sub> (DCM)	T <sub>1</sub> (DCM)
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
PIPOCz	-5.04	-0.89	4.15	3.66	2.71	3.65	2.74
PIPTOCz	-5.01	-0.85	4.16	3.68	2.72	3.64	2.74
PITBOCz	-5.00	-0.85	4.15	3.67	3.12	3.64	2.74
PIFOCz	-5.01	-1.24	3.77	3.26	2.71	3.53	2.74



Fig. 5. Electron Density Contours of frontier molecular orbitals (FMO) of the fluorophores

#### **Electrochemical Properties:**

To better understand the electronic structure (HOMO/LUMO) of synthesized fluorophores, electrochemical properties were evaluated by cyclic voltammetry (CV) analysis. As shown in Fig. 6, all the PI derivatives showed one quasi-reversible redox process around 1.04-1.52 eV, as well as one reversible one-electron oxidation process around 1.15-1.40 eV in CV measurement. These results indicating that all the fluorophores possess good hole and electron transporting properties. Fig. 6 shows that the HOMO energy levels are almost located in the same range and there is no big difference between them. Whereas, the LUMO energy levels of all the fluorophores shown distinguish difference, which would be attributed to the conjugation and deferent substitution at the imidazole group. The HOMO and LUMO energy levels are calculated according to Leeuw *et al.* equations (1) and (2).<sup>70</sup> By using the HOMO/LUMO energy levels we can calculate the band gap of the fluorophores (equations (3)).

$$\mathbf{E}_{HOMO} = -\left(\mathbf{E}_{ox}^{onset} + 4.4\right) \quad \text{eV} \tag{1}$$

$$E_{LUMO} = -\left(E_{red}^{onset} + 4.4\right) \quad eV \tag{2}$$

$$Eg = E_{LUMO} - E_{HOMO} \quad eV \tag{3}$$

The detailed electrochemical data of the synthesized PI derivatives are listed in Table 3. CV investigation revealed that the fluorophores have low-lying energy levels of the lowest unoccupied molecular orbitals (LUMO) ranging from -2.88 eV to -3.35 eV and energy of the highest occupied molecular orbitals (HOMO) ranging from -5.55 eV to -5.80 eV (Fig. 7), suggesting they may possess good electron-transporting and good hole transporting properties. The comparison of HOMO-LUMO energy of all the fluorophores is shown in Fig. 7.



Fig. 6. Cyclic voltammograms of PI derivatives.



Fig. 7. HOMO – LUMO energy gap diagram of all the fluorophores.

Fluorophores	Eoxa	E <sub>red</sub> <sup>b</sup>	НОМО	LUMO	E <sub>g</sub> <sup>c</sup> (eV)	E <sub>g</sub> <sup>d</sup> (eV)
	<b>(V)</b>	(V)	(eV)	(eV)		
PIPOCz	1.168	-1.047	-5.568	-3.353	2.215	2.92
PIPTOCz	1.238	-1.258	-5.638	-3.142	2.496	2.71
PITBOCz	1.158	-1.067	-5.558	-3.333	2.225	2.89
PIFOCz	1.409	-1.520	-5.809	-2.880	2.929	3.05

Table 3. Electrochemical properties of all the fluorophores.

<sup>a</sup> The onset oxidation potential, <sup>b</sup> the onset reduction potential, <sup>c</sup> electrochemical bandgap determined from cyclic voltammetry and <sup>d</sup> optical energy bandgap estimated from the solid-state absorption spectra.

#### **Electroluminescence characteristics:**

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In view of the first-rate photophysical, electrochemical and theoretical studies of all the synthesized PI derivatives, they are adopted as light-emitting emitters to fabricate solution processed doped and nondoped OLED devices. Multilayer OLED devices with and without bipolar host material CBP were fabricated with the configuration of ITO (125 nm)/ PEDOT:PSS (35 nm)/ neat film of PI derivatives (25 nm)/TPBi (35 nm)/LiF (1 nm)/Al and ITO (125 nm)/ PEDOT:PSS (35 nm)/ neat film of PI derivatives doped in CBP host (25 nm)/TPBi (35 nm)/LiF (1 nm)/Al, respectively, In all the fabricated OLED devices PEDOT:PSS and TPBi are work as hole injection and electron-transporting, hole- and exciton-blocking layers, respectively. Lithium fluoride (LiF) was used as a cathode buffer layer for electron injection. The energy level diagram of all the fabricated doped and nondoped OLED devices is shown in Fig. 8.

The current density-voltage-luminance (J-V-L) plots of non-doped and doped devices are shown in Fig. 9 and the significant electroluminescent data are tabulated in Table 4. The EL spectra of the non-doped OLED devices are broad and shifted towards low-energy emission band (higher wavelength) when compared with PL spectra of the respective emitters recorded in DCM solvent. The poor colour purity and performance of the non-doped devices is credited to the unbalanced charge transport and leakage of charge carriers at the interface of respective electrodes without formation of radiative excitons in the desired recombination zone. It also confirmed from the observed high current density and low brightness for the neat device compared to the doped device (Fig. 11). The wide and red shifted EL spectra of the neat devices also suggest the aggregation of molecules in solid state or thin film.

To prevent aggregation prompted fluorescence quenching and boost the EL performance of the compounds, we employed them as emitting dopants in bipolar host matrix CBP and optimized the doping concentrations from 0.5 to 5 wt %. It is interesting to note that the efficiency and luminance of the OLED devices remarkably improved after employing the host matrix CBP. This could be attributed to the balanced charge carriers in recombination zone, effective host to guest energy and possibility of excitons generation on both host and guest. The electronically generated excitons on the CBP host can be successfully captured by the dopant molecules, which also assure the emission originating from the emitters. OLED device consisting of 0.5 wt% doping of PIFOCz as an emitter showed a maximum of EQE 3.3% with CIE coordinates of (0.16, 0.06). For the same doping concentration, PIPOCz based OLED devices showed a maximum EQE of 2.1% and 2.0%, respectively.<sup>49</sup> It is also notable that high doping concentration reduced the device performance and color purity moderately, which may attribute to the crystallinity of molecules and surface morphology of the deposited thin films.<sup>71-74</sup>

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Fig. 8. Schematic illustration of the energy levels of the solution-processed OLED devices The EL spectra of all the fabricated OLED devices are shown in Fig. 10. All the molecules showed near UV-emission with low doping concentration and maxima of emission peaks are centered in between 395-405 nm. The OLED devices consisting of 0.5 wt% of the emitters PIPOCz, PIPTOCz, PITBOCz, and PIFOCz in CBP host matrix displayed CIE coordinates of (0.17, 0.05), (0.18, 0.12), (0.17, 0.07), and (0.17, 0.06), respectively. Figure 11 shows the CIE chromatogram of the device with 0.5 wt% PIPOCz doped in CBP host. The observed CIE coordinates for the developed devices are very close to the standard blue coordinate of National Television Standard Committee (NTSC), i.e. (0.14, 0.08). It is also remarkable that the EL of the compounds is in close resemblance to their PL recorded in DCM solvent, indicating effective charge injection and recombination in the emissive zone. However, the PL spectra of synthesised compounds recorded in DCM solvents and their corresponding EL spectra exhibited multi-peak emission profile at ~400 nm. The reason beside this may be either formation of excimer in solid-state thin film or interfacial exciplex in the developed multi-layered OLED device structure. It is also notable that the solid-state PL spectra of compounds are broad and red shifted as compared to spectra those recorded in solution state. It also contains few extra peaks that may be due to formation of excimer in developed thin films and

intermolecular interaction in packed molecules. The obtained solution processed OLED device efficiency EQE of 3.3% and CIE coordinates of around (0.16, 0.06) are comparable with literature as shown in Table S7.<sup>75-83</sup> All the results reveal that this work provides novel approaches for realizing deep-blue emission fluorescent and pure-white fluorescence-phosphorescence hybrid OLEDs with high performance.



**Fig. 9.** The current density vs voltage (I-V) and Voltage vs luminescence (I-L) plots of the devices a) PIPOCz b) PIPTOCz c) PITBOCz d) PIFOCz

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Fig. 10. EL Spectra of a) PIPOCz b) PIPTOCz c) PITBOCz d) PIFOCz



Fig. 11. CIE chromatogram of the device with 0.5 wt% PIPOCz doped in CBP host.

**Table 4.** Summary of EL performance of solution-processed blue OLEDs-effect of doping concentration on the operating voltage (OV), power efficiency (PE), current efficiency (CE), external quantum efficiency (EQE), CIE coordinates, and maximum luminance of the solution-processed devices with CBP host. [PE, CE, and EQE at 100 cdm<sup>-2</sup> and maximum].

Solution-processed EML		<b>Operation</b> <b>voltage</b>	$\frac{PE_{max}}{CE_{max}} + \frac{EQE_{max}}{CE_{max}} + \frac{1}{CE_{max}} + \frac{1}{C$	$PE_{100}/CE_{100}/EQE_{100}$	CIE <sub>xy</sub> coordinates	Maximum Luminance
Emitter	Emitter	<b>(V)</b>	ImW /cdA /%	IMW /cdA /%		$(cdm^{-2})$
(Dopant)	Concent					
	ration					9
	(wt%)					
PIPOCz	0.5	5.0	0.2/0.2/2.5	0.1/0.2/2.0	(0.17, 0.05)	463
	1	5.0	0.3/0.4/1.9	0.2/0.3/1.8	(0.17, 0.07)	404
	3	5.1	0.4/0.5/1.8	0.2/0.4/1.2	(0.17, 0.09)	375
	5	6.5	0.1/0.2/0.5	0.1/0.1/0.4	(0.17, 0.08)	410
	100	6.7	0.1/0.1/-	_/_/_	-	108
PIPTOCz	0.5	5.0	0.2/0.3/0.6	0.2/0.2/0.5	(0.18, 0.12)	597
	1	4.4	0.4/0.5/1.5	0.3/0.4/1.3	(0.17, 0.08)	462
	3	6.5	0.4/0.7/1.0	0.3/0.6/0.9	(0.17, 0.13)	535
	5	6.6	0.3/0.6/0.8	0.2/0.5/0.8	(0.17, 0.13)	518
	100	-	-	-	-	61
PITBOCz	0.5	6.6	0.1/0.2/1.7	0.1/0.2/0.9	(0.17, 0.07)	393
	1	5.0	0.4/0.5/2.0	0.2/0.4/1.5	(0.17, 0.08)	344
	3	5.4	0.3/0.4/1.3	0.2/0.4/1.1	(0.17, 0.09)	418
	5	6.7	0.1/0.2/0.4	0.1/0.2/0.4	(0.16, 0.09)	523
	100	-	0.1/0.1/-	_/_/_	-	70
PIFOCz	0.5	6.1	0.2/0.4/3.3	0.1/0.2/1.5	(0.17, 0.06)	386
	1	4.2	1.0/1.2/1.5	0.4/0.6/1.5	(0.17, 0.10)	490
	3	5.0	0.4/0.5/1.6	0.3/0.5/1.5	(0.17, 0.09)	426
	5	6.7	0.3/0.5/0.8	0.2/0.4/0.7	(0.17, 0.13)	583
	100	6.7	0.1/0.1/-	_/_/_	-	111

#### **Conclusion:**

In summary, a series of PI derivatives have designed and synthesized. Phenanthroimidazole has been proved with great potential to construct efficient near UV-emission emitters because of its bipolar nature. The different substitution at the N1 position of the imidazole group further influence the optical and electrical properties. The synthesized fluorophores are shown good uscript

thermal stability, near UV-emission (DCM), high photoluminescence quantum yield in the solid state and balance charge transporting characteristics. All the solution processed fabricated OLED devices showed near UV-emission with maxima of EL spectra peaking in between 395-405 nm. Devices using compounds PIFOCz and PIPOCz displayed a maximum external quantum efficiency of 3.3% and 2.5% with CIE coordinates of (0.17, 0.06) and (0.17, 0.05), respectively. It is believed that this work provides novel approaches for realizing near UV-emission or ultra-deep blue fluorescent OLEDs with high performance.

#### **Supporting Information:**

Supporting Information consists of general information about the synthesis and characterisation, synthesis of fluorophores, NMR spectra (<sup>1</sup>H, <sup>13</sup>C <sup>19</sup>F), mass spectra of the luminophores, FT-IR spectra, the CIE chromaticity coordinates for the fluorophores in solutions and solid phase, and Quantum yield studies of fluorophores in solution and solid state, and the calculated UV/Vis absorption spectra and vertical excitation wavelengths, orbital contribution and oscillator strength (f) and atom coordinates of PI derivatives.

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