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Bhausaheb Patil<sup>a</sup>, Jatin Lade<sup>a</sup>, Shian-Sung Chiou<sup>b</sup>, Yen-Chia Cheng<sup>b</sup>, Yi-Fan Lin<sup>b</sup>, Yogesh Jadhav<sup>a</sup>, Prabhakar Chetti<sup>c,\*\*</sup>, Chih-Hao Chang<sup>b,\*\*\*</sup>, Atul Chaskar<sup>a,\*</sup>

<sup>a</sup> National Centre for Nanosciences and Nanotechnology, University of Mumbai, Mumbai, 400098, India

<sup>b</sup> Department of Electrical Engineering, Yuan Ze University, Chung-Li, 32003, Taiwan

<sup>c</sup> Department of Chemistry, National Institute of Technology, Kurukshetra, 136119, Haryana, India

#### ARTICLE INFO

# ABSTRACT

Keywords: Donor-acceptor hybrid Cyanobenzimidazole Carbazole Triphenylamine Green phosphorescent organic light-emitting diodes With a view to attain balanced charge flux for higher device performance of PhOLEDs, we have used carbazole/ triphenyl amine as hole transporting moiety and cyano along with benzimidazole as electron transporting core in 3-Cbz-ImdCN, 4-Cbz-ImdCN and TPA-ImdCN. Their thermal, photophysical and electrochemical properties have been evaluated to shed light on structure-property-performance relationship. Good performances have been exhibited by these bipolar host materials in green PhOLEDs with maximum external quantum efficiencies were observed in the range of 5.3–11.5% using Ir(ppy)<sub>3</sub> emitter. Further, 3-Cbz-ImdCN hosted orange and red PhO-LEDs with the Ir(MDQ)<sub>2</sub>acac and Ir(piq)<sub>2</sub>acac emitters revealed the external quantum efficiencies of 5.1% and 6.3%, respectively. In all the devices pure emission was observed from dopants only which clearly implies that the devices possess effective energy transfer from the host to the guest.

## 1. Introduction

Organic light-emitting diodes (OLED) perceived a massive heed in the lighting, displays and printed electronic industries owing to their low power consumption and roll to roll printing [1–5]. Hence, current OLED research efforts are focused on enhancement of device stability and efficiency with simplified device architecture. In conventional OLED, light is emitted by singlet excitons leading to internal quantum efficiency (IQE) up to 25% as exciton possess singlet: triplet ratio as 1:3. The significant development in OLED research was design and development of phosphorescent organic light-emitting diodes (PhOLEDs). The electrophosphorescence can proficiently utilize both singlet as well as triplet excitons to reach internal quantum efficiency (IQE) to ideal level i.e., 100% [6-8]. The transition metal-centred phosphorescent emitter used for this purpose convert singlet excitons to triplet excitons through inter system crossing by means of spin-orbital interaction. Albeit, phosphorescent emitter needs to be doped in suitable host material to suppress the aggregation quenching and triplet-triplet annihilation of emitters [9]. Nevertheless, the host materials must have higher

triplet energy than that of emitter to ensure exothermic energy transfer and well confined triplet exciton formation on the dopant, good energy level alignment with the neighboring functional layers, it should promote balanced charge fluxes, and good thermal and morphological stabilities to prevent morphological changes of the amorphous organic layer upon heating [10-14]. Initially the unipolar hosts, viz. hole-transporting material comprising electron-donating moiety and electron-transporting material encompassing electron-withdrawing moiety have been employed for hosting phosphorescent dopant. Unfortunately, they promoted unbalanced charge flux which leads to narrow charge recombination zone as recombination zone moves near to hole transporting layer (HTL) or electron transporting layer (ETL) resulted into exciton diffusion and triplet-triplet annihilation. Owing to this researcher focused their attention on development of tailor-made bipolar host materials by wise selection and proper linking of holeand electron-transporting moieties which could endorse balanced charge flux to accomplish highly efficient phosphorescent organic light-emitting diodes (PhOLEDs) [15-25]. The photophysical, electrochemical, and thermal properties of bipolar host materials could be

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<sup>\*</sup> Corresponding author.,

<sup>\*\*</sup> Corresponding author.

<sup>\*\*\*</sup> Corresponding author.

E-mail addresses: chetti@nitkkr.ac.in (P. Chetti), chc@saturn.yzu.edu.tw (C.-H. Chang), achaskar25@gmail.com, achaskar@nano.mu.ac.in (A. Chaskar).

tuned by changing linking spacer, topology, and donor: acceptor ratio [26–28].

Hitherto, abundant classes of bipolar host materials have been reported encompassing carbazole, indolocarbazole, and aryl amine moieties as hole-transporting units owing to their excellent hole-mobilities and favorable triplet energy ( $E_T$ ) [29–33] while oxadiazole, benzimidazole, pyridine, phenanthroline, phosphine oxide, phosphine sulfide, etc. as electron-transporting units [34–47]. Notably, CBP is the most frequently used carbazole-based host having a triplet energy ( $E_T$ ) of 2.56 eV. While, its structural analog mCP exhibited elevated triplet ( $E_T$ ) of 2.9 eV which promoted it extensive use as host for all color emitters for phosphorescent OLEDs [48–54]. More recently, Z. Gao et al. reported diphenylquinoxaline-based host materials M1 and M2 for red phosphors whereas, Su and coworkers developed new bipolar hosts *o*-PQPC, *m*-PQPC, and *p*-PQPC which displayed maximum current of 21.9 cd/A, power efficiency of 15.4 lm W<sup>-1</sup>, and external quantum efficiency of 12.2% [55,56].

Nevertheless, cyano moiety is also extensively used *n*-type electrontransporting unit in the design and synthesis of bipolar host molecules. Notably, Zhang and co-workers reported a bipolar unit CBP-CN which showed enhanced activity for red and green PhOLEDs as compare to commonly used green host CBP [57]. Lee et al. used a CN as a ubiquitous unit for their molecules and they exhibited maximum external quantum efficiency (EQE) of 23.8% for fluorescent and 26.7% for PhOLEDs [58]. Liao L.-S. et al. demonstrated carbazole based novel host compounds i.e., CNPhCz and DCNPhCz which hold elevated energies and appropriate HOMO/LUMO energy states, thus CNPhCz hosted devices revealed maximum EQE of 17.1% and 24.4%, respectively [59]. Recently, same group reported dibenzo[a,c]phenazine materials by introducing cyano groups into dibenzo[a,c]phenazine and showed progressive performance of device with the maximum EQE of 23.24% [60]. Although, the host materials involving either heterocycles or cyano groups are now much familiar, but the grouping of heterocycles with cyano as new *n*-type building blocks are rarely reported [61]. Since last couple of decades researchers across the globe put forward their efforts to develop highly efficient PhOLEDs which led to the development of novel bipolar host materials with reasonable thermal stability and high triplet energy showing efficiency (EQE) up to 30% [62].

Herein, we wish to report novel bipolar hosts 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN comprising carbazole/triphenylamine as hole-transporting functional unit (donor) and cyanobenzimidazole as an electron-transporting moiety (acceptor). When cyano or benzimidazole core used independently in bipolar hybrid their electron mobility failed to match the hole mobility of donor core. Therefore, here we used combination of two to enhance the electron mobility of bipolar host. A concise strategy was applied to tune the photophysical, thermal and



Scheme 1. Synthetic pathway and chemical structures of bipolar host materials 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN.

electrochemical properties, and shed light on structure-propertyperformance relationship. Eventually these molecules were used for fabrication of green PhOLEDs and the external quantum efficiencies of 11.5%, 11.4% and 5.3% were observed for 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN hosted devices, respectively. Further, 3-Cbz-ImdCN hosted orange and red PhOLED devices were also fabricated and they revealed the external quantum efficiencies of 5.1% and 6.3%, respectively.

#### 2. Results and discussion

#### 2.1. Synthesis

Scheme 1 depicts the synthetic pathway we have followed to articulate the bipolar host materials 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN. 3-Formyl-N-phenylcarbazole synthesized from N-phenylcarbazole using Vilsmeier-Haack reaction [63,64], on condensation with 3,4-diaminobenzonitrile offered 2-(9-phenyl-9-H-carbazol-3-yl)-1H-benzo[d]imidazole-5-carbonitrile (3-Cbz-ImdCN) in 72% yield. Carbazole on reaction with 4-fluorobenzaldehyde in presence of potassium tert-butoxide offered 4-(9H-carbazol-9-yl) benzaldehyde which on condensation with 3.4-diaminobenzonitrile vielded 2-(4-(9H-carbazol-9-yl) phenyl)-1H-benzo[d]imidazole-5-carbonitrile (4-Cbz-ImdCN) in 68%. Triphenylamine of Vilsmeier-Haack reaction gave 4-(diphenylamino) benzaldehyde which on condensation with 3, 4-diaminobenzonitrile furnished 2-(4-(diphenylamino) phenyl)-1-H-benzo[d]imidazole-5-carbonitrile (TPA-ImdCN) in 78%. All the products were purified by column chromatography and final three molecules were further purified by sublimation for device fabrication. The chemical structures of all the synthesized molecules were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra and mass spectral data.

#### 2.2. Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to characterize the thermal properties of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN (Fig. 1, Table 1). The glass transition temperature ( $T_g$ ) of 89 °C and 78 °C were observed for 4-Cbz-ImdCN and TPA-ImdCN, respectively. Whereas decomposition temperature for 3-Cbz-ImdCN, 4-Cbz-ImdCN and TPA-ImdCN were found at 390 °C 218 °C and 354 °C, correspondingly. The high values of glass transition ( $T_g$ ) and decomposition temperature ( $T_d$ ) implies that they are proficient of enduring vacuum thermal sublimation and suppress an aggregation formation with preserving amorphous nature of thin film [65,66].

## 2.3. Photophysical properties

Electronic absorption (UV-Vis) and photoluminescence (PL) spectra

of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN in dichloromethane (DCM) at room temperature are displayed in Fig. 2. All these molecules exhibit absorption peak around 325–375 nm owing to  $\pi$ - $\pi$ \* transition. These long wavelength  $\pi$ - $\pi$ \* electronic transition is attributed to extended  $\pi$  conjugation. Further, the red shift absorption in polar solvent as compare to nonpolar solvent (Fig. 3) suggest that the Franck-Condon excited states are subject to large changes in dipole moment with respect to the ground state. The PL spectra of these molecules are observed around 392–458 nm. The red shift emission in polar solvent (Fig. 3) implies involvement of rapid photo-induced electron transfer (PET) which leads to a large change in the dipole moment in the excited state. Apparently, the triplet energies ( $E_{\rm T}$ ) of 2.71, 2.62 and 2.46 eV were determined for 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN from the highest energy peaks of the phosphorescence spectra (Fig. 4).

## 2.4. Electrochemical properties

Cyclic voltammetry measurements of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN were performed using a CHI 619B potentiostat. 3-Electrode cell system encompassing a glassy carbon electrode as working electrode, silver/silver chloride (Ag/AgCl) as reference electrode and a platinum wire as counter electrode was used. A ferrocene (Fc) was used as an internal standard for cyclic voltammetry while tetrabutylammonium hexafluorophosphate (TBAPF6 0.1 M) in DCM and tetrabutylammonium perchlorate (TBAP, 0.1 M) in THF were used as the supporting electrolyte for oxidation and reduction scan, respectively. The oxidation potential arises from carbazole/triphenyl amine while reduction potentials arise from cyanobenzimidazole (Fig. 5). The irreversible oxidations were observed owing to dimerization or electropolymerization of carbazole/triphenyl amine. The lower oxidation potential detected for 3-Cbz-ImdCN as compare to 4-Cbz-ImdCN was assigned to higher degree of  $\pi$ -conjugation. Apparently, the reduction on-set of 4-Cbz-ImdCN is at higher potential as compare to 3-Cbz-ImdCN, implying the electron distribution on their lowest unoccupied molecular orbital (LUMO) is solely confined on the cyanobenzimidazole. The HOMO energy levels were found out from the first oxidation peak of onset potential of  $(E_{ox}^{onset})$  by the mathematical equation of  $E_{HOMO} = -e$ (E<sub>ox</sub><sup>onset</sup> + 4.4) [67,68] for 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN is as -5.65, -5.71 and -5.74 eV respectively. Similarly, the LUMO energy levels were intended by the first reduction peak of onset potential  $(E_{red}^{onset})$  from the calculation by  $E_{LUMO} = -e (E_{ox}^{onset} + 4.4)$  [69] to be as -3.31 eV, -3.32 eV and -3.68 eV. The band gap between the LUMO and HOMO was found to be 2.28 eV, 2.39 eV, and 2.06 eV for these molecules.

# 2.5. Theoretical studies



Molecular simulations for the reported molecules 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN were carried out using DFT and TDDFT

Fig. 1. TGA and DSC thermograms of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN observed at 10 °C min<sup>-1</sup> heating rate.

#### Table 1

Physical properties of 3-Cbz-ImdCN, 4-Cbz-ImdCN and TPA-ImdCN.

	$\lambda_{abs.}^{a}$ (nm)	$\lambda_{\rm fluor.}^{b}$ (nm)	$E_{\rm T}^{\rm c}$ (eV)	HOMO (eV)	LUMO <sup>d</sup> (eV)	$E_{g}^{e}$ (eV)	$T_{\rm d}^{\rm f}$ (°C)	$T_g^g$ (°C)
3-Cbz-ImdCN	344	392	2.71	-5.65	-3.31	2.28	390	-
4-Cbz-ImdCN	356	434	2.62	-5.71	-3.32	2.39	218	89
TPA-ImdCN	366	458	2.46	-5.74	-3.68	2.06	354	78

<sup>a</sup> Absorption maximum.

<sup>b</sup> Fluorescence maximum.

<sup>c</sup> Triplet energy at 77 K.

<sup>d</sup> LUMO is find out via eq. LUMO = HOMO +  $E_g$ .

<sup>e</sup> Estimated from the absorption onset;

 $^{\rm f}$  T<sub>d</sub>, thermal decomposition temperature;

<sup>g</sup> T<sub>g</sub>, glass transition temperature.



Fig. 2. Room-temperature absorption and emission (PL) spectra of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN in DCM.

methods with G16 quantum chemical package [70,71] Ground state molecular geometries are obtained at the B3LYP level with the standard basis set 6-31G (d, p). The calculated vibrational spectrum in all the optimized structures has no imaginary frequencies, which indicates that all the optimized structures are located at the minimum point of the potential energy surface. Electronic absorption properties were carried out using the TDDFT (TD-B3LYP/6-31G (d, p) methodologies for the optimized geometries and frontier molecular orbitals responsible for the excitations leading to the absorption maximum, were pictorially visualized from the population analysis.

To get more insight in to the absorption energies, we have carried out TDDFT calculations for the reported molecules. The calculated absorption energies along with major transitions are tabulated in Table 2. The experimental absorption ( $\lambda_{exp}$ ) of molecules 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN are 344 nm, 356 nm and 366 nm respectively; while their calculated absorption energies are 330 nm, 379 nm and 372 nm respectively, which indicates a fair agreement of calculated results with experimental one within the limitation. In all the three molecules the excitations are from HOMO to LUMO. From FMO analysis, the HOMO orbital of 4-Cbz-ImdCN is mainly distributed on carbazole where as in 3-Cbz-ImdCN it is localised at carbazole with little contribution from cyanobenzimidazole. Further in TPA-ImdCN it is situated at triphenyl as well as benzimidazole. On the other hand, the LUMO of 4-Cbz-ImdCN is populated on cyanobenzimidazole and phenyl ring of Nphenyl carbazole while in 3-Cbz-ImdCN it is situated on cyanobenzimidazole and little on carbazole. However, in TPA-ImdCN LUMO energy level is distributed on cyanobenzimidazole and phenyl ring linked to it (Fig. 6). The clear spatial separation of HOMO and LUMO energy levels in 4-Cbz-ImdCN implies that the HOMO-LUMO excitation would shift the electron density distribution from carbazole to cyanobenzimidazole which polarize excited state.

Further, to get the geometrical parameters in its excited states,

excited state geometries of these molecules were optimized at TD-B3LYP method with 6–31G (d, p) basis set. The dihedral angle between carbazole and phenyl ring in ground and excited state for 3-Cbz-ImdCN and 4-Cbz-ImdCN were found to be -57.95, -51.66 and -49.29, -89.71, respectively. Whereas, in TPA-ImdCN those were observed as -33.07 and -94.63, correspondingly (shown in Table 3). However, the dihedral angle between donor carbazole/triphenyl amine and acceptor cyanobenzimidazole in ground and excited state for 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN were found as -177.18, -08.00, -07.56 and -177.31, -0.01, -0.51, respectively. The difference between dihedral angle was caused due to substitution pattern as well as steric effect. The twisting between these three molecules and their non-planar confirmations can efficiently hinder the unnecessary intramolecular charge transfer and  $\pi$ - $\pi$  stacking, which are a typical requirement for efficient OLEDs devices.

#### 2.6. Reorganization energies

According to hopping model, charge transfer reaction is selfexchange electron transfer reaction between neutral and radical cation (hole transfer) shown in equation 1

$$M + M^+ \to M^+ + M \tag{1}$$

Marcus expresses the rate constant (K) for charge transfer reaction between two molecules shown in equation (2) as [72,73].

$$K = \left(\frac{4\pi^2}{h}\right) H^2 (4\pi\lambda kT)^{-1/2} exp\left(-\lambda/4kT\right)$$
(2)

Here, *H* is charge transfer integral matrix between neighboring molecules [74,75],  $\lambda$  is reorganization energy, *k* is Boltzmann constant and *T* is the temperature. Total reorganization energy is sum of internal and external reorganization energies, however external  $\lambda$  is negligible as



Fig. 3. Room-temperature absorption and emission (PL) spectra of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN in DCM and toluene.

compared to internal  $\lambda$ . The calculation of internal  $\lambda$  is done by using the following equations [76,77].

$$\lambda_h = \lambda_1 + \lambda_2 = [E^+(M_0) - E^+(M_+)] + [E^0(M_+) - E^0(M_0)]$$
(3)

$$\lambda_e = \lambda_3 + \lambda_4 = [E^-(M_0) - E^-(M_-)] + [E^0(M_-) - E^0(M_0)]$$
(4)

Here,  $\lambda_1$  is the energy difference between the energy of cation (obtained at ground state neutral molecule  $E^+(M_0)$ ) and energy of cation molecule in its lowest energy geometry  $(E^+(M_+))$ ,  $\lambda_2$  is the energy difference between the energy of neutral molecule (obtained at optimized cationic state  $E^0(M_+)$ ) and energy of a neutral molecule in its lowest energy geometry  $(E^0(M_0))$  (shown in equation (3)). Similarly,  $\lambda_3$  is energy difference between the energy of anion (obtained at ground state

neutral molecule  $E^{-}(M_{0})$ ) and energy of anion molecule in its lowest energy geometry ( $E^{-}(M_{-})$ ),  $\lambda_{4}$  is energy difference between the energy of neutral molecule (obtained at optimized anionic state  $E^{0}(M_{-})$ ) and energy of neutral molecule in its lowest energy geometry ( $E^{0}(M_{0})$ ) (shown in equation (4)).

The calculated hole  $(\lambda_h)$  and electron  $(\lambda_e)$  reorganization energy for the reported molecules are shown in Table 4. As evident from equation (2), smaller reorganization energy led to the higher rate constant value which in turns increases the charge transport properties in the molecule. From Table 4, 4-Cbz-ImdCN is showing smallest  $\lambda_h$  value of 124 meV, while 3-Cbz-ImdCN and TPA-ImdCN are showing 181 meV and 128 meV respectively. Similar is the case for  $\lambda_e$  values, 4-Cbz-ImdCN is showing 313 meV and TPA-ImdCN being the highest (468 meV). Moreover, in all



Fig. 4. Room-temperature emission (PL) and low temperature Phosphorescence (Phos.) spectra of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN in toluene.



Fig. 5. Cyclic voltammogram of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN.

**Table 2** Calculated absorption in nm ( $\lambda$ ), strength of oscillator (*f*), main transitions (MT), and %weight (Ci) at B3LYP/6-31G (d, p) level.

Name $\lambda_{Cal}$ f         MT         %6           3-Cbz-ImdCN         330         0.653         H $\rightarrow$ L         90           4-Cbz-ImdCN         379         0.456         H $\rightarrow$ L         98           TDA L=date         272         0.046         H $\rightarrow$ L         98					
3-Cbz-ImdCN         330 $0.653$ $H \rightarrow L$ 90           4-Cbz-ImdCN         379 $0.456$ $H \rightarrow L$ 98           TDA $L = dN$ 272 $0.456$ $H \rightarrow L$ 98	Name	$\lambda_{\text{Cal}}$	f	MT	%Ci
$1PA-IIIIdCN$ $3/2$ $0.948$ $\Pi \rightarrow L$ 98	3-Cbz-ImdCN 4-Cbz-ImdCN TPA-ImdCN	330 379 372	0.653 0.456 0.948	$\begin{array}{l} H \rightarrow L \\ H \rightarrow L \\ H \rightarrow L \end{array}$	90 98 98

the three molecules  $\lambda_h < \lambda_e$ , suggesting the studied molecules are better candidate for hole transport material rather than electron transport materials. Also, The  $\lambda_h$  calculated for the isomers are smaller than that of N, N'-diphenyl-N, N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine

(TPD) which is typical hole transport material ( $\lambda_h = 290 \text{ meV}$ ) [78]. In conclusion the theoretical calculations show that the studied isomers are showing smaller hole reorganization energy than standard molecule reported in literature. Also, the synthesized isomers are showing very small hole reorganization energy suggesting these isomers are better candidate for hole transport materials.

#### 2.7. OLED device

In the context of promising physical properties, we decided to investigate the bipolar host properties of newly synthesized carbazole/ triphenylamine-cyanobenzimidazole hybrid materials (3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN) for green PhOLEDs. We fabricated device with typical multi-layer architecture of ITO/TAPC doped with 20 wt % MoO<sub>3</sub> (10 nm)/TAPC (15 nm)/TCTA (5 nm)/Host doped with 8 wt% Ir(ppy)<sub>3</sub> (30 nm)/B3PyMPM (50 nm)/LiF (0.8 nm)/Al (120 nm). The thicknesses of the p-doped hole-injection layer (HIL), HTLs, and ETLs in the aforementioned devices were cautiously adjusted to improve the radiation output and carrier balance. 3-Cbz-ImdCN was employed as a host for device A, 4-Cbz-ImdCN for device B, and TPA-ImdCN for device C while heavy-metal complex  $Ir(ppy)_3$  was used as an emitter. The ptype conductivity dopant MoO<sub>3</sub> was introduced into 1,1-bis[(di-4-tolylamino)phenyl]cvclohexane (TAPC) to enhance conductivity and hole injection, while intrinsic TAPC was used to prevent excitons quenching by conductivity dopant [79]. 4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA) was used as the HTL [80], 4,6-Bis(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PyMPM) was used as the ETL while LiF and Al were used as the electron injecting layer and cathode, correspondingly. Furthermore, TCTA was inserted between TAPC and the emitting layer (EML) to reduce the excessive energy barrier between host material and TAPC. The chemical structures of the materials used for device fabrication and device architecture employed are shown in Fig. 7 while EL spectra of devices, current density-voltage-luminescence characteristics, external quantum efficiency, luminance efficiency, and power efficiency versus luminance are revealed in Fig. 8. All the device performances are summarized in Table 5.

The EL spectra of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN, hosted devices showed pure emission from green dopant Ir(ppy)<sub>3</sub> only (Fig. 8a). The pure emission suggests that all tested devices possess effective energy transfer from the host to the guest. Furthermore, the diffusion of high-energy excitons located in the EML to adjacent layers was significantly reduced. Current density-voltage-luminescence (J-V-L) characteristics of devices A, B, and C are revealed in Fig. 8b. Clearly, device C exhibits a higher current density than those of devices A and B, which might the result of the relatively lower HOMO level of TPA-ImdCN. Hence, the turn-on voltages of devices A and B are slightly higher than that of device C. Nevertheless, the maximum luminance of device A with 3-Cbz-ImdCN shows the highest value of 64303 cd  $m^{-2}$ , which is about 2.5 times that of device C and about 1.4 times that of device B. The much higher luminance obtained in device A illustrates that 3-Cbz-ImdCN has great stability at high current density. Notably, external quantum efficiencies and luminance/power efficiencies of the three devices are shown in Fig. 8c and d, respectively. From Fig. 8 and Table 5, the peak efficiencies accomplished are 11.5%, 39.0 cd  $A^{-1}$ , 43.3  $\textrm{lm}\,\textrm{W}^{-1}$  for device A, 11.4%, 39.3 cd  $\textrm{A}^{-1},$  46.8  $\textrm{lm}\,\textrm{W}^{-1}$  for device B, and 5.3%, 18.3 cd  $A^{-1}$ , 17.9 lm  $W^{-1}$  for device C. Furthermore, at a high luminance of  $100 \text{ cd m}^{-2}$ , the external quantum efficiencies of devices A, B, and C respectively maintained efficiency levels of 10.8%, 10.9%, and 5.3%; hence, they exhibited efficiency drops of only 6%, 4%, and 0% from their respective peak values to those recorded at 100 cd  $m^{-2}$ . All tested devices retained high efficiency at high luminance levels and showed negligible efficiency roll-off. Overall, the tested green PhOLEDs presented great EL performance, which raises the feasibility of using the carbazole/triphenylamine-cyanobenzimidazole hybrid bipolar host materials in commercial applications.

Further, 3-Cbz-ImdCN hosted orange and red PhOLEDs with the



Fig. 6. Frontier molecular orbitals of 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN calculated with DFT on a B3LYP/6-31G (d, p) level.

architecture of ITO/TAPC doped with 20 wt% MoO<sub>3</sub> (10 nm)/TAPC (30 nm)/3-Cbz-imdCN with 8 wt% Ir(piq)<sub>2</sub>acac or 2 wt% Ir(MDQ)<sub>2</sub>acac (30 nm)/Bebq2 (50 nm)/LiF (0.8 nm)/Al (120 nm) were also fabricated (Fig. 9). Fig. 10 shows the EL characteristics of the tested devices, and Table 6 summarizes the corresponding numerical data. The EL spectra of OLEDs showed emission from orange and red dopants (Fig. 10a) which suggests that both the devices possess effective energy transfer from the host to the guest. Nevertheless, the EL spectrum of the orange OLED shows a small BeBq<sub>2</sub> emission peak, indicating that the exciton formation zone is located near the EML/ETL interface. This phenomenon might be the result of the low doping concentration of Ir(MDQ)<sub>2</sub>acac. Current density-voltage-luminescence (J-V-L) characteristics of orange and red devices are shown in Fig. 10b. As indicated, the low turn-on voltage of 2.7 V obtained in the red device (Ir(piq)<sub>2</sub>acac) shows that 3-Cbz-ImCN has excellent carrier transport capability. The efficiencies curves of the orange and red devices are shown in Fig. 10c and d. The orange and red devices exhibited the maximum external quantum efficiencies of 5.1% and 6.3%, respectively (Table 6). These results indicate that 3-Cbz-ImdCN has application potential as the host material of orange and red PhOLEDs.

#### 3. Materials and methods

All the chemical reagents were brought from commercial resources. All the reactions were performed in a Borosil round bottom flask and monitored by TLC, aluminum plates (0.25 mm, E. Merck) precoated with silica gel (Merck 60 F-254). TLC plates were envisaged under a short-as well as long wavelength UV lamp. The reactions were escorted in open air atmosphere in presence of solvents like MeOH, EtOH and DMF. Yields mention to spectroscopically (<sup>1</sup>H, <sup>13</sup>C NMR) homogeneous material found after column chromatography implemented on silica gel (100-200 mesh size) provided by S.D. Fine and Sigma Aldrich Chemicals Limited, India. <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> as well as DMSO solution with an Agilent 300/400 MHz spectrometer. Chemical shift ( $\delta$ ) values were quoted in ppm, comparative to SiMe<sub>4</sub> ( $\delta = 0.0$ ) as an internal standard. The number of protons (n) for a specified resonance is indicated by nH. Peak multiplicities are labeled by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; J, coupling constant in Hz (S6). Melting points were recorded on a standard melting point apparatus from Gautam lab equipment, Mumbai and are uncorrected. Electronic absorption spectra values were note down on UV-Vis-NIR spectrophotometer. Emission spectra were recorded on Varian Cary-Eclipse fluorescence spectrophotometer. Thermal study was dignified on PerkinElmer system with a

#### Table 3

Dihedral angles of the molecules in ground state and excited state.



#### Table 4

Calculated hole  $(\lambda_h)$  and electron  $(\lambda_e)$  reorganization energies (in meV).

Name	$\lambda_{\mathbf{h}}$	$\lambda_{e}$
3-Cbz-ImdCN	181	313
4-Cbz-ImdCN	124	377
TPA-ImdCN	128	468

 $20~^\circ\text{C/min}$  heating rate and 20~mL/min  $N_2$  flow. Electrochemical readings were carried out using CH electrochemical analyzer with a 100~mV/ s scan rate. HOMO and LUMO energy values were calculated from the oxidation and reduction peak potentials.

#### 1. Thin film and device fabrication

The indium-tin-oxide (ITO)-coated glass substrates (sheet resistance  ${\sim}15~\Omega~\text{sq}^{-1}$ ) was cleaned in an ultrasonic bath by deionized water and acetone in series for 20 min, followed by warmed in methanol for about 10 min. The washed ITO glass substrate was then used with UV-ozone to eliminate residual organic impurities. Organic materials were purchased from Shine Materials Technology. All organic materials were subjected to temperature gradient sublimation. EL device was equipped by vacuum deposition in a base pressure of  $1~\times~10^{-6}$  torr. The hole-transporting, electron transporting, and emitting layers were placed sequentially at a rate of 0.1 nm/s. The cathode, 0.8-nm-thick LiF, and 120-nm-thick Al was then set down at a rate of 0.02 nm/s and 0.5 nm/s, respectively, through shadow mask (2  $\times$  2 mm<sup>2</sup>) without breaking the vacuum.

#### 2. Thin film and device characterization

The thicknesses of organic layers were acquired with a SOPRA ellipsometer. Current density-voltage-luminance (*J-V-L*) characteristics of the devices were performed in a glove-box using two Keithley 2401 source measure units equipped with a calibrated Si photodiode. EL spectra of the devices were recorded using an Ocean Optics USB2000 spectrometer. On the basis of the favorable results from photophysical investigation, thermal, electrochemical, DFT and physical study, it is

clear that all the materials possess promising characteristics that can allow them to serve as a host of phosphorescent dopants due to their appropriate HOMO/LUMO energy level.

#### 3.1. Preparation of 9-phenyl-9H-carbazole-3-carbaldehyde (2)

POCl<sub>3</sub> (2.30 mL, 24.7 mmol) was added dropwise to DMF (14.6 mL, 189.0 mmol) under stirring at 0 °C. The resulting mixture was stirred at 0 °C for 4 h and then warmed to room temperature. To this mixture 9-phenyl-9*H*-carbazole 1 (5.0 g, 20.5 mmol) was added. The reaction mixture was heated to 90 °C and stirred for 7 h. The solution was poured into an ice-bath, neutralized with sodium bicarbonate and extracted with DCM (3 × 40 mL). The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue obtained was purified with column chromatography on 100: 200 mesh silica gel by using 20% ethyl acetate in *n*-hexane as the eluent to afford compound 2 as a white solid (4.40 g, 79%).

mp 108–110 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36–7.41 (distorted q, *J* = 8.0, 7.0 Hz, 2H), 7.43–7.49 (m, 2H), 7.52–7.56 (m, 3H), 7.65 (t, *J* = 8.0, 7.5 Hz, 2H), 7.94–7.96 (dd, *J* = 9.0, 1.5 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.68 (s, 1H), 10.12 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 110.09, 110.40, 120.65, 121.18, 123.22, 123.58, 123.82, 126.98, 127.18, 127.44, 128.32, 129.45, 130.11, 136.71, 141.87, 144.50, 191.71; ESI-MS: *m*/*z* 272.02 [M + H]<sup>+</sup>.

#### 3.2. Preparation of 4-(9H-carbazol-9-yl) benzaldehyde (5)

To a stirred solution of carbazole 3 (6.30 g, 37.7 mmol) in anhydrous DMF (150 mL) was added potassium *tert*-butoxide (4.23 g, 37.7 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was heated to 110 °C and then a solution of 4-fluorobenzaldehyde 4 (4.04 mL g, 37.7 mmol) in anhydrous DMF (10 mL) was added dropwise into the mixture over 50 min. The mixture was kept at 110 °C for 36 h. Then the mixture was cooled to room temperature and poured into 500 mL ice water. The precipitate obtained was filtered, dried and recrystallized by using acetone/water (v/v = 9:1) system to afford compound 5 as a pale yellow solid (6.15 g, 60%).

mp 156–158 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33 (t, J = 7.0 Hz,



Fig. 7. (a) Chemical structures of the materials used; (b) device architecture employed in this work.

2H), 7.44 (t, J = 8.0, 7.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 7.5 Hz, 2H), 8.15 (t, J = 7.5, 7.0 Hz, 4H), 10.12 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 109.75, 120.49, 120.80, 123.97, 126.27, 126.84, 131.37, 134.65, 140.07, 143.41, 190.95; ESI-MS: <math>m/z$  272.03 [M + H]<sup>+</sup>.

#### 3.3. Preparation of 4-(diphenylamino) benzaldehyde (7)

To a stirred solution of triphenylamine 6 (8.0 g, 32.6 mmol) in DMF (16 mL) was added dropwise POCl<sub>3</sub> (15.2 mL, 163.0 mmol) at 0 °C. After completion of addition, the reaction mixture was warmed to room temperature and then heated to 45 °C for 2 h. The solution was poured into an ice-bath and neutralized with sodium carbonate. The resulting precipitate was filtered, dried and recrystallized from ethanol to afford compound 7 as a pale yellow solid (8.20 g, 92%).

mp 120–122 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.02 (d, J = 8.5 Hz, 2H), 7.16–7.18 (m, 6H), 7.34 (t, J = 7.5 Hz, 4H), 7.68 (d, J = 8.0 Hz, 2H), 9.81 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 119.34, 125.09, 126.30, 129.11, 129.71, 131.28, 146.15, 153.35, 190.40; ESI-MS: *m*/*z* 274.13 [M + H]<sup>+</sup>.

# 3.4. Preparation of 2-(9-phenyl-9H-carbazol-3-yl)-1H-benzo[d] imidazole-5-carbonitrile (3-Cbz-ImdCN)

To a stirring solution of 3,4-diaminobenzonitrile (8) (1.5 gm) in MeOH, (100 mL), solution of 9-phenyl-9H-carbazole-3-carbaldehyde (2) was added dropwise through a dropping funnel. After complete addition the reaction mass was refluxed for 10–12 h. After completion of the reaction, the reaction mixture was allowed to cool at room temperature and poured into water. The precipitate obtained was filtered, washed with water and dried. The solid was purified with column chromatography on 100: 200 mesh silica gel by using Petroleum ether: DCM (9:1) to afford the pure product 3-Cbz-ImdCN as a pale yellow solid (1.02 g, 72%).

<sup>1</sup>H NMR (500 MHz, DMSO):  $\delta = 13.54$  (s, 1H), 9.14 (s, 1H), 8.37–8.31 (m, 1H), 8.27–8.21 (m, 1H), 8.14 (s, 1H), 8.04–7.84 (m, 1H), 7.78–7.69 (m, 2H), 7.64–7.59 (m, 2H), 7.56–7.49 (m, 2H), 7.43–7.35 (m, 2H), 7.30–7.25 (m, 1H), 7.22–7.13 (m, 1H); <sup>13</sup>C NMR (125 MHz, DMSO): 158.0, 155.8, 141.9, 141.4, 136.8, 130.8, 128.6, 127.5, 127.3, 127.1, 126.0, 125.8, 123.6, 123.1, 121.6, 121.3, 121.2, 120.6, 120.1, 119.3, 110.7, 110.5, 104.1; ESI-MS: *m/z* 384.4418 [M + H]<sup>+</sup>.

# 3.5. Preparation of 2-(4-(9H-carbazol-9-yl) phenyl)-1H-benzo[d] imidazole-5-carbonitrile(4-Cbz-ImdCN)

To a stirring solution of 3,4-diaminobenzonitrile (8) (1.5 gm) in MeOH, (100 mL) solution of 4-(9H-carbazol-9-yl) benzaldehyde (5) was added dropwise through a dropping funnel. After complete addition the reaction mass was refluxed for 10–12 h. After completion of the reaction as indicated by TLC, the reaction mixture was cooled and poured into water. The precipitate obtained was filtered, washed with water and dried. The mixture was purified with column chromatography on 100: 200 mesh silica gel by using petroleum ether: DCM (9:1) to afford the pure product 4-Cbz-ImdCN as a pale yellow solid (0.96 g, 68%).

<sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  = 13.69 (s, 1H), 8.52 (d, *J* = 10 Hz, 1H), 8.33–8.21 (m, 3H), 8.11 (d, *J* = 10 Hz, 1H), 7.90 (d, *J* = 10 Hz, 1H), 7.81 (d, *J* = 10 Hz, 1H), 7.67–7.63 (m, 1H), 7.54 (d, *J* = 10 Hz, 1H), 7.50–7.46 (m, 2H), 7.40–7.31 (m, 3H), 7.15 (t, *J* = 10 & 15 Hz, 1H); ESI-MS: *m/z* 384.4419 [M + H]<sup>+</sup>.

# 3.6. Preparation of 2-(4-(diphenylamino) phenyl)-1H-benzo[d] imidazole-5-carbonitrile (TPA-ImdCN)

To a stirring solution of 3,4-diaminobenzonitrile (8) (1.5 gm) in MeOH (100 mL), solution of 4-(diphenylamino) benzaldehyde (7) was added dropwise through a dropping funnel. After complete addition the reaction mass was refluxed for 10-12 h. After completion of the



Fig. 8. EL characteristics of the phosphorescent OLEDs: (a) normalized EL spectra; (b) current density-voltage-luminance (*J-V-L*) curves; (c) external quantum efficiency vs luminance; (d) luminance efficiency/power efficiency vs luminance for devices A, B, and C.

 Table 5

 EL Characteristics of green PhOLEDs with different host materials.

Device	А	В	С	
Host		3-Cbz- ImdCN	4-Cbz- ImdCN	TPA-ImdCN
External Quantum	Peak	11.5	11.4	5.3
Efficiency (%)	$10^2 \text{ cd}$	10.8	10.9	5.3
	$m^{-2}$			
Luminance Efficiency	Peak	39.0	39.3	18.3
$(cd A^{-1})$	$10^2 { m cd} { m m}^{-2}$	36.7	37.5	18.2
Power	Peak	43.3	46.8	17.9
Efficiency ( $\text{Im W}^{-1}$ )	$10^2  ext{ cd}$ $m^{-2}$	30.3	33.5	16.8
Turn-on Voltage (V)	$1 \text{ cd} m^{-2}$	2.7	2.5	2.4
Maximum Luminance (cd m <sup>-2</sup> ) [V]		64303	45713	25337
		[11.8 V]	[11.8 V]	[10.4 V]
CIE coordinate (x, y)	$10^2 \text{ cd}$ m <sup>-2</sup>	(0.37, 0.59)	(0.37, 0.59)	(0.36, 0.59)
	$10^3  ext{ cd}$ $ ext{m}^{-2}$	(0.37, 0.59)	(0.37, 0.59)	(0.36, 0.60)

reaction, the reaction mixture was cooled and poured into water. The precipitate obtained was filtered, washed with water and dried. The mixture was purified with column chromatography on 100: 200 mesh silica gel by using petroleum ether: DCM (9:1) to afford the pure product 4-Cbz-ImdCN as a pale yellow solid (1.11 g, 78%).

<sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  = 13.3 (s, 1H), 8.07 (d, *J* = 5.0 Hz, 1H), 7.88–7.83 (m, 1H), 7.73–7.56 (m, 1H), 7.44–7.34 (m, 3H), 7.28–7.23 (m, 2H); 7.17–7.11 (m, 3H), 7.05–6.93 (m, 4H); ESI-MS: *m*/*z* 386.1533 [M + H]<sup>+</sup>.

# 4. Conclusion

We succeeded in design and synthesis of three bipolar host materials 3-Cbz-ImdCN, 4-Cbz-ImdCN, and TPA-ImdCN employing carbazole/ triphenylamine as donor and cyanobenzimidazole as an acceptor. Here we have used cyano and benzimidazole as electron transporting moieties because in most of the bipolar host materials hole mobility is always higher than electron mobility when donor: acceptor ratio is 1:1. The tuning in linking topology leads to alteration in photophysical, thermal, and electrochemical properties which eventually affect the device performance, as exhibited by 3-Cbz-ImdCN and 4-Cbz-ImdCN. Among the three host materials, 3-Cbz-ImdCN hosted green device exhibited best performance with external quantum efficiency of 11.5%, luminance efficiency 39 cd  $A^{-1}$  and power efficiency of 43.3 lm  $W^{-1}$  with maximum luminance of 64303 cd m<sup>-2</sup> at 11.8 V. 3-Cbz-ImdCN hosted orange and red PhOLED devices were also fabricated and interestingly red device revealed the maximum external quantum efficiency of 6.3%. We strongly believe that the present work will promote cyanobenzimidazole as potential electron transporting motif in the molecular designing of bipolar host materials for efficient phosphorescent organic light-emitting diodes.



Fig. 9. (a) Chemical structures of the materials used; (b) device architecture of the orange and red OLEDs. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 10. EL characteristics of the phosphorescent OLEDs: (a) normalized EL spectra; (b) current density-voltage-luminance (*J-V-L*) curves; (c) external quantum efficiency vs luminance; (d) luminance efficiency/power efficiency vs luminance for devices O and R.

#### Table 6

EL Characteristics of orange and red phosphorescent OLEDs with 3-Cbz-imdCN host.

Device	0	R Ir(piq) <sub>2</sub> acac	
Emitter	Ir(MDQ)2acac		
External Quantum Efficiency	Peak	5.1	6.3
(%)	$10^2 \text{ cd}$ m <sup>-2</sup>	4.8	5.5
Luminance Efficiency (cd $A^{-1}$ )	Peak	11.0	5.9
	$10^2 \text{ cd}$ m <sup>-2</sup>	10.2	5.2
Power	Peak	11.6	6.6
Efficiency ( $lm W^{-1}$ )	$10^{2} \text{ cd} \\ \text{m}^{-2}$	7.5	3.9
Turn-on Voltage (V)	$1 \text{ cd } \text{m}^{-2}$	2.9	2.7
Maximum Luminance (cd m <sup>-2</sup> ) [	22444 [15.6 V]	14999 [16.8 V]	
CIE coordinate (x, y)	$10^2  ext{ cd}$ m <sup>-2</sup>	(0.56, 0.42)	(0.67, 0.32)
	$10^3  cd$ m <sup>-2</sup>	(0.56, 0.42)	(0.67, 0.33)

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2021.106090.

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