Derivatives of Cyanonaphthyl-Substituted Phenanthroimidazole as Blue Emitters for Nondoped Organic Light-Emitting Diodes

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ABSTRACT: New multifunctional blue-emissive materials with superior thermal properties, viz., 4,4′-bis(1-(4-naphthyl)-1H-phenanthro[9,10-d]imidazol-2-yl)binaphthyl (NPIBN), 4,4′-bis(1-(4-cyanonaphthyl)-1H-phenanthro[9,10-d]imidazol-2-yl)binaphthyl (CNIPBN), and 4,4′-bis(1-(4-cyanonaphthyl)-1H-phenanthro[9,10-d]-imidazol-2-yl)binaphthyl (CNIPBN) have been synthesized. The said molecules show high photoluminescence quantum yield (Φs) of 7.46/7.56 cd A−1 and ηex 4.96/5.4% at low turn-on voltage (3.5/3.8 V). Nondoped devices based on D–π–A architecture, 4-(2-(5-(9H-carbazol-9-yl)thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)naphthalene-1-carbonitrile exhibit maximum efficiencies (ηex 2.32%; ηp 3.42 lm W−1; ηc 2.01%; η3 3.89 cd A−1; η5 3.15 lm W−1) compared to 4-(2-(5-(4-(di phenylamino)phenyl)thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)naphthalene-1-carbonitrile (ηex 2.01%; ηc 3.89 cd A−1; η3 3.15 lm W−1).

1. INTRODUCTION
Development of efficient blue emitters with balanced carrier injection as well as transporting characteristics in organic light-emitting devices (OLEDs) remains a challenging task because of the higher energy gap (Eg) results in low electron affinities, thereby lowering the efficiency. Because of the higher energy gap (Eg) results in low electron affinities, thereby lowering the efficiency. Though nondoped blue devices based on the diphenylethene emitter (CIE: 0.15, 0.11) and anthracene derivative (CIE: 0.14, 0.12) show high external quantum efficiencies (ηex) of 5.2 and 5.3%, respectively, their power (ηp) and current (ηc) efficiencies are low because of the large band gap (Eg). The large band gap impedes injection of charge carriers to the emissive layer (EML). A blue device with an oligoquinoline EML shows high ηp (power efficiency) and ηex (external quantum efficiency). The simple structured device of bis(phenanthroimidazolyl)biphenyl derivative exhibits higher performance (CIE y 0.15; ηex 6.31%) than multilayered devices because of the large electron injection barrier. Because cyanostub substitution could limit the ability to transport hole to adjust carrier injection, it is aimed to incorporate the cyanonaphthyl at side capping of the phenanthroimidazole ring.

Thermally activated delayed fluorescence (TADF), hybridized local and charge-transfer (HLCT), and triplet–triplet annihilation (TTA: ηlat of 62.5%) in fluorescent OLEDs enhanced the internal quantum efficiency (ηlat) because of small ΔEST (singlet–triplet energy splitting) in reverse intersystem crossing (RISC) (Scheme 1). The donor–spacer–acceptor (D–π–A) compounds with HLCT show high exciton utilization efficiency (ηS), and this is attributed to the hot exciton model. The ηex and ηS are

Scheme 1. Effect of TADF and HLCT on 100% Exciton Utilization Efficiency (ηS)

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obtained using $\eta_{EQE} = \eta_{EQE} \times \eta_{out} = \eta_{out} \times \eta_{S} \times \eta_{PL} \times \eta_{rec}$ and $[\eta_{S} = \eta_{out} \times \eta_{PL} \times \eta_{rec} \eta_{EL}]$ respectively (Scheme 1). The LE predominates HLCT affords high $\eta_{PL}$, and predominates CT in HLCT is the cause for small $\Delta E_{ST}$. The bipolar phanthrimidazoles are excellent pure blue-emissive materials. Here, we present a novel method to develop cyanosubstituted blue-emitting molecules, namely, 4,4′-bis[(4-cyanonaphthyl)-1H-phenanthro[9,10-d]imidazole (BNPINCN), and 4,4′-bis[(4-cyanonaphthyl)-1H-phenanthro[9,10-d]imidazole-1-carbonitrile (TPNCN-TPA) and a weak donor in 4-(2-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1H-carbazole (CuI, K2CO3, 18-crown-6 (1H & 13C), mass spectrometry, and elemental analysis, respectively. The bromo intermediates (BNPINCN, BNPINCN, and CNPIBN), and donor−π−acceptor compounds (TPNCN-TPA and TPNCN-Cz) were characterized by NMR ($^1H$ & $^{13}C$), mass spectrometry, and elemental analysis, respectively.

2. RESULTS AND DISCUSSION

2.1. Molecular Design. The synthetic route of bis phenanthrimidazole derivatives, namely, NPIBN, CNPIBP, and CNPIBN, and donor−acceptor derivatives, TPNCN-TPA and TPNCN-Cz are presented in Scheme 2. The key intermediates, 2-(1-bromonaphthalen-4-yl)-1-(naphthalen-1-yl)-1H-phenanthro[9,10-d]imidazole (BNPINCN), 4-(2-(4-bromophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)-naphthalene-1-carbonitrile (BPINCN), 4-(2-(1-bromonaphthalen-4-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)-naphthalene-1-carbonitrile (BNPINCN), and 4-(2-(5-bromo-thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)-naphthalene-1-carbonitrile (BTPINCN) have been synthesized with yield of 65−70%. The bis phanthrimidazole derivatives, namely, NPIBN, CNPIBP, and CNPIBN were prepared from the intermediates BNNPI, BPNICN, and BTPINCN, respectively, by homocoupling reaction (100 °C, 24 h). The bromo intermediate BTPINCN on reaction with diphenylaminophenyl boronic acid [Pd(PPh3)4, Na2CO3, toluene: ethanol for 18 h] or 9H-carbazole (CuI, K2CO3, 18-crown-6 for 18 h) yielded TPNCN-TPA and TPNCN-Cz, respectively. The bromo intermediates (BPNICN, BTPINCN, and BTPINCN), bis phanthrimidazoles (NPIBN, CNPIBP, and CNPIBN), and donor−π−acceptor compounds (TPNCN-TPA and TPNCN-Cz) were characterized by NMR ($^1H$ & $^{13}C$), mass spectrometry, and elemental analysis, respectively.}

![Scheme 2. Synthetic Route of CNPIBP, NPIBN, CNPIBN, TPNCN-TPA, and TPNCN-Cz](image-url)
the phenanthrimidazole plane and the bibhenyl/binaphthyl bridge attached to imidazole carbon), and B-θ° (between two biphenyl/binaphthyl centers) which play a key role in the overlap of the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) MOs in ground as well as excited states (Figure 1). The ground-state energy results by a potential energy scan reveal that N-θ° is limited at room temperature (k_B T, 12.5 meV) (CNPIBP—50.0°–120.0°; CPIBN—50.0°–130.0°; C-θ° (99.0°–130.1°); B-θ° (CNPIBP—88.7°–128.5°; CPIBN—100.0°–130.0°) and increases sharply when the twist angle goes out of the range (Figure 2a). Hence, the extent of conjugation was restricted and wave function of the two phenanthrimidazoles shows a comparatively minimized overlap of biphenyl/binaphthyl spacer and the location of C-θ° (230°) (NPIBN) and B-θ° (40.0°) (NPIBN) providing large electron overlap among the biphenyl/binaphthyl bridge at C2 and phenanthrimidazole.43 The incorporation of the cyanonaphthyl group in the phenanthrimidazole unit increases the charge transfer state; as a result, the efficient reverse intersystem crossing process would be facilitated to enhance the fraction of singlet generation.43 Biphenyl (CNPIBP) and binaphthyl (CPIBN) between the two phenanthrimidazole groups in the backbone enhanced the horizontal locally excited state to balance the CT component, resulting in high photoluminescence quantum yield (Φ_s).44 Clipping the linkage between the two phenanthrimidazole planes by biphenyl or binaphthyl is beneficial to suppress the aggregation effect to maintain the color purity of OLEDs. In D–π–A materials, ground state (S₀) geometry, naphthonitrile part (θ₁), as well as thiophene moiety (θ₂) are largely twisted over phenanthrimidazole. The dihedral angles are 58.1° (θ₁) and 26.9° (θ₂) for TPNCN-TPA and 50.2° (θ₁) and 22.7° (θ₂) for TPNCN-Cz. The TPA of TPNCN-TPA and Cz of TPNCN-Cz are twisted, and the dihedral angles are 160.2° and 169.1°, respectively.45 The large twist angles of rigid TPNCN-Cz is due to a strong repulsive interaction of the two hydrogens of carbazole with hydrogens of the binaphthyl ring. The twist angles (θ₁) of excited TPNCN-Cz and TPNCN-TPA are increased (38.6° and 28.0°) on comparison to the twist angle of S₀. In the same way, the excited state twist angle (θ₂) was small for TPNCN-Cz (68.9°) and TPNCN-TPA (60.2°). The TPNCN-Cz and TPNCN-TPA bond lengths (R₁) are increased (0.03 and 0.07 Å, respectively) on moving from ground (S₀) to excited states (S₁). On switching from ground (S₀) to excited (S₁) state geometry; small structural modification of TPNCN-Cz increases the photoluminescence efficiency (ηPL).46–49 These orthogonal dihedral angles confirmed the noncoplanar twisting conformation of NPIBN, CNPIBP, CPIBN, TPNCN-TPA, and TPNCN-Cz which suppresses the red shift and harvested

Figure 1. Ground-state and excited-state geometries with a dihedral angle of CNPIBP, NPIBN, CPIBN, TPNCN-TPA, and TPNCN-Cz.
high \( \eta_{\text{ex}} \) in the film by restraining the intermolecular interaction.\textsuperscript{46–49}

### 2.3. Thermal and Electrochemical Properties

Thermal characteristics of bis phenanthroimidazoles and donor–acceptor molecules were studied using thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) techniques. The incorporation of a highly rigid bulky moiety at imidazole carbon and side capping at imidazole nitrogen enlarged the size and improved their thermal stability which is required for efficient devices (Table 1; Figure 3). All materials show high thermal stability. Their 5% weight-loss temperature \( T_d \) ranges from 430 to 556 °C (CNPIBP—540 °C, NPIBN—520 °C, CNPIBN—556 °C, TPNCN-Cz—448 °C, TPNCN-TPA—430 °C). Such high \( T_d \) as well as \( T_g \) shows that the amorphous layers of these compounds can be fabricated by vacuum thermal evaporation technology. In addition, the said materials are expected to exhibit high morphological stability which is desirable for OLEDs.\textsuperscript{9e} High \( T_d \) reveals that the said materials are suitable for device fabrication. Further, all the materials show high \( T_g \) at 239−241 °C, showing improved morphological stability because of a rigid phenanthrimidazole core. The higher \( T_g \) implicates a stable film on thermal evaporation and reduces the likelihood of phase separation on heating, enhancing the device lifetime and so forth among the donor–acceptor compounds, TPNCN-Cz exhibits higher thermal stability \( T_g \)—161 and \( T_d \)—448 °C compared to TPNCN-TPA 156 \( T_g \) and 430 °C \( T_d \) (Figure 3): stronger rigidity is likely to be a

#### Table 1. Photophysical and Thermal Properties and Device Efficiencies

| Parameters | CNPIBP | NPIBN | CNPIBN | TPNCN-TPA | TPNCN-Cz |
|------------|--------|-------|--------|------------|----------|
| \( T_g/T_d \) (°C) | 221/540 | 239/520 | 241/556 | 156/430 | 161/448 |
| \( \lambda_{\text{abs}} \) (nm) \( (\text{abs/bs}) \) | 261, 340/266, 341 | 255, 334/258, 335 | 258, 336/260, 338 | 254, 308/252, 316 | 250, 301/246, 295 |
| \( \Phi \) (\text{soln/film}) | 0.85/0.76 | 0.75/0.68 | 0.90/0.88 | 0.71/0.62 | 0.78/0.72 |
| \( \tau \) (ns) | 1.92 | 1.87 | 2.01 | 5.4 | 4.3 |
| \( \lambda_{\text{em}} \) (nm) \( (\text{em/em}) \) | 430/442 | 428/435 | 425/438 | 408/436 | 400/420 |
| \( E_g \) (eV) | \(-3.09\) | \(-3.02\) | \(-3.00\) | \(-2.88\) | \(-2.73\) |
| \( k_c \times 10^3 \) (s\(^{-1}\)) | 4.4 | 4.0 | 4.5 | 1.3 | 1.6 |
| \( k_n \times 10^3 \) (s\(^{-1}\)) | 0.8 | 2.1 | 0.5 | 0.55 | 0.73 |
| \( \text{EOMO–LUMO (eV)} \) | \(-5.48/2.39\) | \(-5.50/2.48\) | \(-5.52/2.42\) | \(-5.30/2.56\) | \(-5.35/2.62\) |

\textsuperscript{a}Normalized absorption (\( \lambda_{\text{abs}} \)) and emission (\( \lambda_{\text{em}} \)) spectra CNPIBP, NPIBN, CNPIBN, TPNCN-TPA, and TPNCN-Cz in CH\(_2\)Cl\(_2\) \( (10^{-5}\) M)/film.

\textsuperscript{b}\( T_g/T_d \)—glass transition temperature/thermal decomposition temperature at a weight percentage of 95%.

\textsuperscript{c} \( \Phi \) (soln/film)—PL quantum yield was calculated in dichloromethane/solid state quantum yield has been measured on the quartz plate using an integrating sphere.

\textsuperscript{d}HOMO–LUMO—\( E_{\text{HOMO}} = E_{\text{ox}} + 4.8 \text{ eV}/E_{\text{LUMO}} = E_{\text{HOMO}} − 1239/\lambda_{\text{onset}} \)–\( E_g \)—energy gap (HOMO–LUMO).

Figure 2. (a) PES at different twist angles C-\( \theta \), B-\( \theta \), and N-\( \theta \) of CNPIBP, NPIBN, and CNPIBN (inset: B-\( \theta \)) and PES of excited states of (b)TPNCN-TPA; (c)TPNCN-Cz with increasing solvent polarity.
reason for the observed results. The improved $T_\phi$ is because of the C–N–H/C–N···π interaction of the cyano group with the phenanthroimidazole core. This induces molecular packing in the film. The thermal morphological stability of the thin film of these compounds was studied using atomic force microscopy (AFM) at about 30 and 90 °C (12 h). The rms roughness values of NPIBN-0.20 nm, CNPIBP-0.25 nm, CNPIBN-0.21 nm, TPNCN-TPA-0.27 nm, and TPNCN-Cz-0.23 nm film surfaces reveal the absence of remarkable modifications before and after annealing. This supports the adoptability of these molecules for fabrication (Figure 3). The injection of holes in the interface between the layers in OLEDs is essential for the efficient functioning of devices: shallow $E_{\text{HOMO}}$ of EML enhances the hole injection in OLEDs. The frontier energies support the ability of electron injection by bis phenanthroimidazole. New-born emitters exhibit similar characteristics.

**5.48 eV (CNPIBP), and 5.52 eV (CNPIBN) have been calculated**. The calculated $E_{\text{LUMO}}$ ($E_{\text{LUMO}} = 1239/\lambda_{\text{onset}}$) −2.48 eV (NPIBN), −2.39 eV (CNPIBP), and −2.42 eV (CNPIBN) are approximately of the same value of TPBi. This supports the ability of electron injection by bis phenanthroimidazoles CNPIBP, CNPIBN, and CNPIBN. The HOMO is mainly located on cyanonaphthyl with the biphenyl bridge in NPIBN and cyanonaphthyl and with the biphenyl bridge in CNPIBP and CNPIBN, whereas the LUMO is located on the imidazole core with the biphenyl bridge in NPIBN and the imidazole ring and with the biphenyl bridge in CNPIBP and CNPIBN (Figure 4): separation of charges in these molecules benefit injection of charges from electrodes. Partial overlap of HOMO–LUMO on the phenanthroimidazole ring supports the charge transfer from the π-linked biphenylphenanthroimidazole/biphenylphenanthroimidazole group to the cyano-naphthyl moiety, and the long π-linkers are beneficial to enhance the quantum yield. The calculated radiative ($k_r$) and nonradiative ($k_{nr}$) decay constants are ($k_r/k_{nr}$) 4.0/2.1 ns (NPIBN); 4.4/0.8 ns (CNPIBP), and 4.5/0.5 ns (CNPIBN) (Figure 3). The radiative rate was increased for binaphthyl-bridged CNPIBP and CNPIBN with a simultaneous decreasing nonradiative rate on comparison with biphenyl-bridged NPIBN. The HOMO orbital is distributed over triphenylamine in TPNCN-TPA ($E_{\text{HOMO}}$ = −5.30 eV) and carbazole in TPNCN-Cz ($E_{\text{HOMO}}$ = −5.35 eV), whereas the LUMO orbital localized on the cyanonaphthyl fragment at the nitrogen atom ($E_{\text{LUMO}}$ = −2.56 eV TPNCN-TPA; −2.62 eV TPNCN-Cz) (Figure 4). The HOMO and LUMO of D–π–A compounds display adequate separation features, and the differences are quite small which benefit hole as well as electron transportation (bipolar properties); this lowers singlet–triplet splitting ($\Delta_{ST}$). Hence, the HOMO and LUMO moieties individually undertake the electron and hole transport functions. The calculated electron/hole transfer integrals of TPNCN-Cz (0.25/0.42 eV) and TPNCN-TPA (0.24/0.50 eV) reveal that these materials are bipolar materials. These molecules show both redox potentials indicating their charge transport abilities.

**2.4. Photophysical Properties and HLCT Character.** The optical characteristics of emissive materials were studied in solution as well as solid by absorption and emission studies (Figure S1: Table 1). When the cyano group is incorporated, the modification in the CT state will cause red-shifted absorption and emission. The strong absorption at ∼250 nm due to π–π* transition originates from the phenyl ring to the imidazole ring. In addition, the absorption at 300–340 nm is attributed to intramolecular CT from the donor to acceptor unit. Compared with parent compounds bis phenanthrimidazoles (NPIBN, CNPIBP, and CNPIBN), D–π–A materials (TPNCN-TPA and TPNCN-Cz) show larger absorption intensity. This is ascribed to the newly generated CT owing to conjugation among the donors (triphenylamine or carbazole) and acceptor (phenanthroimidazole) as the donor moieties attached to the para carbon of thiophenyl phenanthroimidazole. New-born emitters exhibit similar
absorption (sol/film) 254 (ε_{max} = 39 370 cm⁻¹ M⁻¹), 308/252, 316 (TPNCN-TPA), and 250 (ε_{max} = 40 000 cm⁻¹ M⁻¹), 301/246, 295 nm (TPNCN-Cz) because the core fragment is not different. The absorption from 301 and 308 nm is due to intramolecular charge transfer from the donor (carbazole/triphenylamine) to acceptor (phenanthrimidazole). The intramolecular charge transfer is further confirmed by molecular electrostatic potential (Figure 4). Compared with solution, the small red shift shown by the film shows suppression of π-π* stacking. The emission of NPIBN, CNPIBP, and CNPIBN is observed at 435, 442, and 438 nm, respectively, in solid [full width half-maximum (fwhm) ≈ 30 nm], the red shift is unlikely due to aggregation but may be because of excited-state conformational change. The incorporated −CN group rarely influences the electronic properties as well as band gap. It is in accordance with quantum chemical calculations. The phenanthrimidazole derivatives NPIBN, CNPIBP, CNPIBN, TPNCN-TPA, and TPNCN-Cz show blue emission at 428, 430, 425, 408, and 400 nm, respectively (Figure S1), and the emission peak is red-shifted by increase of solvent polarity (Figure S2). This variation is because of polarization-induced optical shift. The calculated singlet energy/triplet energy (E_{S}/E_{T}) of NPIBN (2.7/2.3 eV), CNPIBP (2.8/2.3 eV), and CNPIBN (2.9/2.3 eV) shows that they have high triplet energy to sensitize phosphorescent dopants with E_{T} below 2.3 eV. The PL spectra gradually widened and their peaks show red shift with increase of solvent polarity which indicates that their excited state have strong CT character when compared to the ground state and further stabilized by polar solvents. Compared to TPNCN-TPA, TPNCN-Cz shows higher blue shift of absorption as well as emission. This is ascribed to low-electron donation of Cz compared to TPA. The increased % LE along with decreased % CT in S_{1} HLCT is probably the reason for the observed blue shift. The FWHM of the absorption peak of TPNCN-Cz (30 nm) is reduced compared to TPNCN-TPA (42 nm). This result shows decrease of % CT of TPNCN-Cz in S_{1}, which is in accordance with natural-transition orbitals (NTO) analysis (S_{0} → S_{1} transition). The emission peak of TPNCN-TPA as well as TPNCN-Cz gives blue shift compared to parent molecules. This is contradictory to the widely observed red shift due to π-conjugation. The overlap of UV with PL spectra is due to the increased % LE in TPNCN-TPA and TPNCN-Cz compared to their parent molecules. The TPNCN-Cz shows solvatochromic smaller red shift in emission (32 nm) compared to that of TPNCN-TPA (56 nm) (Figure S2; Tables S1 and S2). In the same way, a small absorption red shift viz., 20 and 28 nm, is observed for TPNCN-Cz and TPNCN-TPA (Figure S3; Tables S1 and S2). Solvatochromic shift confined that low-lying S_{1} excited state must possesses CT character. The CT % in S_{1} state of TPNCN-Cz is less than TPNCN-TPA, whereas LE % of TPNCN-Cz is larger than TPNCN-TPA (Table S3). In S_{0} → S_{1} and S_{0} → S_{2} transitions, the HLCT was composed of the CT state followed by the LE state and exhibited larger oscillator strength [f_{S_{0}−S_{1}}/f_{S_{0}−S_{2}} = 0.684/0.6712 (TPNCN-Cz—Figure S4): 0.3792/0.3673 (TPNCN-TPA—Figure 5)] compared with other S_{0}→S_{n} transitions. This is because of larger LE % in HLCT (Table 2—TPNCN-Cz and Table 3—TPNCN-TPA) which is necessary for higher energy (E_{S}/E_{T}) of NPIBN, CNPIBP, and CNPIBN.

Figure 4. Optimized geometry with LE and CT directions, HOMO, and LUMO and molecular electrostatic potential surface of CNPIBP, NPIBN, CNPIBN, TPNCN-TPA, and TPNCN-Cz.

Figure 5. NTO pairs and transition character analysis for singlet and triplet states of TPNCN-TPA (% oscillator strength and % weights of hole-particle).
efficiency OLEDs. The hole as well as particle of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in TPNCN-Cz and TPNCN-TPA consist of two different configurations with comparable contributions: $C_i$ direction takes up one and $N_i$ direction takes up other: LE and HLCT states have one syruct each (Figure S1). This implies that these compounds show a well-mixed CT and LE. In D–π–A molecules, CT and LE components are mutually perpendicular in HLCT. This mixed state leads to lowering of oscillator strengths in TPNCN-TPA, ($f_{S_0 \rightarrow S_1} = 0.3792$) than that of TPNCN-Cz ($f_{S_0 \rightarrow S_1} = 0.6814$) with small energy of transition (0.04 eV) from $S_1$ to $S_2$. This transition among the excited states suppresses nonradiative decay, increasing both the efficiency of photoluminescence and oscillator strength. This is supported by optical studies.

### 2.5. Solvatochromism for HLCT Character.

From the Lipper–Mataga plot (SI-I; Figure S1, Tables S1 and S2), the dipole moment of the $S_0$ ($\mu_S$) state of TPNCN-Cz and TPNCN-TPA could be estimated as 5.0 and 6.34 D in low-polar solvents. This is ascribed to LE transition and $\mu_S$ in high polar solvents is 22.9 and 24.1 D, respectively. The large $\mu_S$ in high polar solvent is close to $\mu_D$ of the CT molecule, DMABN (23.0 D). This indicates the domination of CT and LE in more and less polar solvents, respectively, and mixed LE and CT contribution in medium polar solvents. A potential energy scan of TPNCN-Cz and TPNCN-TPA excited state shows that the $S_1$ state remained unchanged with increasing solvent polarity, whereas the $S_0$ state decreased to intercross with the $S_1$ state at moderate polarity and to be much lower than the $S_1$ state at high polarity (Figure 2bc). This shows that HLCT is only emissive state in TPNCN-Cz and TPNCN-TPA to Cz increases LE % in HLCT and improves PL (%PL) of TPNCN-Cz. To supplement experimental observations, DFT and Multiwfn calculations were made to probe excited-state characteristics. NTO (Figure 5 TPNCN-TPA and TPNCN-Cz—Figure S4; Tables 2 and 3), hole particle distribution (Figure S5; Table S4—TPNCN-Cz, Figure S6; Table S5—TPNCN-TPA), transition density matrix (TDM) TPNCN-Cz and TPNCN-TPA: Figure 6-TPNCN-Cz and Figure S7.

### Table 2. Computed [Zindo (Singlet or Triplet, n States = 10)] Singlet ($E_S$) and Triplet ($E_T$) Energies (eV), Oscillator Strength ($f$), Dipole Moment ($\mu$, D) and Singlet–Triplet Splitting ($\Delta E_{ST}$, eV) of TPNCN-Cz from NTOs

| energy level | $E_S$ | oscillator strength ($f$) | $\mu$ | NTO transitions | $E_T$ | $\Delta E_{ST}$ | NTO transitions |
|--------------|-------|--------------------------|------|-----------------|------|----------------|-----------------|
| 1            | 3.15  | 0.6814                   | 1.1769| 109 $\rightarrow$ 111 | 1.19 | 1.96     | 108 $\rightarrow$ 110 |
| 2            | 3.30  | 0.6712                   | 1.0205| 108 $\rightarrow$ 110 | 1.26 | 2.04     | 109 $\rightarrow$ 111 |
| 3            | 3.49  | 0.1818                   | 0.8360| 108 $\rightarrow$ 111 | 1.64 | 1.85     | 109 $\rightarrow$ 112 |
| 4            | 3.55  | 0.0043                   | 0.7749| 108 $\rightarrow$ 113 | 1.96 | 1.59     | 109 $\rightarrow$ 114 |
| 5            | 3.60  | 0.1488                   | 0.7272| 109 $\rightarrow$ 115 | 2.12 | 1.48     | 109 $\rightarrow$ 113 |
| 6            | 3.68  | 0.2139                   | 0.6451| 109 $\rightarrow$ 110 | 2.23 | 1.35     | 108 $\rightarrow$ 118 |
| 7            | 3.90  | 0.0994                   | 0.4232| 109 $\rightarrow$ 112 | 2.27 | 1.63     | 109 $\rightarrow$ 110 |
| 8            | 4.17  | 0.0872                   | 0.1551| 107 $\rightarrow$ 111 | 2.36 | 1.81     | 109 $\rightarrow$ 110 |
| 9            | 4.22  | 0.0444                   | 0.1055| 107 $\rightarrow$ 114 | 2.49 | 1.73     | 109 $\rightarrow$ 115 |
| 10           | 4.32  | 0.1183                   | 0.0116| 109 $\rightarrow$ 112 | 2.78 | 1.54     | 109 $\rightarrow$ 118 |

### Table 3. Computed [Zindo (Singlet or Triplet, n States = 10)] Singlet ($E_S$) and Triplet ($E_T$) Energies (eV), Oscillator Strength ($f$), Dipole Moment ($\mu$, D), and Singlet–Triplet Energy Difference ($\Delta E_{ST}$, eV) of TPNCN-TPA from NTOs

| energy level | $E_S$ | oscillator strength ($f$) | $\mu$ | NTO transitions | $E_T$ | $\Delta E_{ST}$ | NTO transitions |
|--------------|-------|--------------------------|------|-----------------|------|----------------|-----------------|
| 1            | 3.09  | 0.3792                   | 0.8004| 124 $\rightarrow$ 126 | 1.21 | 1.88     | 122 $\rightarrow$ 126 |
| 2            | 3.35  | 0.3673                   | 0.5349| 123 $\rightarrow$ 125 | 1.32 | 2.03     | 122 $\rightarrow$ 125 |
| 3            | 3.44  | 0.0710                   | 0.4540| 122 $\rightarrow$ 125 | 1.54 | 1.90     | 124 $\rightarrow$ 127 |
| 4            | 3.52  | 0.0433                   | 0.3735| 124 $\rightarrow$ 125 | 1.69 | 1.83     | 119 $\rightarrow$ 133 |
| 5            | 3.59  | 0.0330                   | 0.3039| 122 $\rightarrow$ 126 | 1.81 | 1.76     | 118 $\rightarrow$ 134 |
| 6            | 3.64  | 0.0433                   | 0.2450| 123 $\rightarrow$ 131 | 2.00 | 1.64     | 119 $\rightarrow$ 135 |
| 7            | 3.69  | 0.1729                   | 0.2043| 124 $\rightarrow$ 125 | 2.13 | 1.56     | 118 $\rightarrow$ 133 |
| 8            | 3.74  | 0.1003                   | 0.1496| 122 $\rightarrow$ 128 | 2.36 | 1.38     | 122 $\rightarrow$ 134 |
| 9            | 3.86  | 0.1748                   | 0.0336| 123 $\rightarrow$ 126 | 2.45 | 1.41     | 122 $\rightarrow$ 133 |
| 10           | 3.89  | 0.0281                   | 0.0280| 124 $\rightarrow$ 131 | 2.46 | 1.43     | 122 $\rightarrow$ 134 |
TPNCN-TPA), root-mean-square deviation (RMSD), $H$ and $t$ indexes, centroid of hole ($h^+$) and electron ($e^-$), excitation energy (eV), $\Delta r$ index, hole ($h^+$) and electron ($e^-$) overlap, charge transfer and dipole moment, and so forth are displayed in Tables 4, S4−S9 and Figures 5, 6, S4−S8 and discussed in SI-II. The density of overlap among the particle and hole depends upon the configuration of donor−acceptor architecture, and the magnitude of overlap intensity tuned the % LE and % CT in S1 state.

2.6. Quasi-Equivalent Hybridization. The excited states ($S_1$ and $S_2$) of TPNCN-Cz and TPNCN-TPA show a hybrid-splitting character because of interstate-coupling of CT and LE to form HLCT (Figure 4; Tables 2 and 3). This interstate hybridization-coupling of positive and negative combination of CT with LE wave functions are shown in the equation:

$$\Psi_{S_1/S_2} = c_{LE} \Psi_{LE} \pm c_{CT} \Psi_{CT}.$$ 

The CT of TPNCN-Cz (60%) is lower than TPNCN-TPA (90%) because of poor donor capacity of Cz compared to TPA (Table S3). Hence, TPNCN-Cz is expected to show larger photoluminescence efficiency ($\eta_{PL}$) and blue-shift the emission compared to TPNCN-TPA. Thus, both $S_1$ and $S_2$ are to be taken as the hybrid state because of the CN group in TPNCN-Cz and TPNCN-TPA. The $S_1$ and $S_2$ are approximately of same energy ($E$), oscillator strength ($f$), and hole particle distribution (Tables 2 and 3). This suggests a quasi-equivalent hybridization among CT and LE. In contrast, in nonequivalent hybridization, the $S_1$ and $S_2$ have different energies, $f$, and so forth, and quasi-equivalent hybridization provides high $\eta_{PL}$ as well as high $\eta_s$ and EL efficiencies because of comparable CT % and LE % in HLCT (Figure S9). The formation of the HLCT state is analyzed using energies of excitation of CT and LE states. A wide band gap between $T_2$ and $T_1$ of TPNCN-Cz (1.23 eV) and TPNCN-TPA (0.56 eV) stems from phenanthrimidazole (acceptor). The $E_g$ of TPNCN-Cz (Table 2) is wider than that of TPNCN-TPA (Table 3). A small $\Delta E_{ST} \approx 0$ ($E_{S_1} - E_{T_2}$) favors RISC ($T_2 \rightarrow S_1$) because of HLCT’s nature. As a result of increased LE % in $S_1$ of TPNCN-Cz high photoluminescence efficiency ($\eta_{PL}$), high exciton utilization efficiency ($\eta_s$) and high external quantum efficiency ($\eta_{ex}$) have been harvested compared to TPNCN-TPA. The LE % and CT % in HLCT tuned the PL and EL of the film: higher CT % enhances $\eta_s$ by RISC because of small $\Delta E_{ST}$ and lowers $\eta_{PL}$. Hence, modulation of excited state composition is employed by using different components in the D−π−A molecules with the biphenyl/binaphthyl bridge to achieve high $\eta_s$ ($<\text{CT} %$) and high $\eta_{PL}$ ($<\text{LE} %$) in HLCT which leads to quasi-equivalent hybridization. Efficient quasi-equivalent hybridization depends on both $E_{LE} - E_{CT}$ band gap and interstate-coupling strength. In TPNCN-Cz and TPNCN-TPA, the $E_{LE} < E_{CT}$ and band gap ($E_{S_1} - E_{S_2}$) is small relative to parent compounds and leads to quasi-hybridization. In TPNCN-Cz, the $E_{S_1} - E_{S_2}$ is reduced more when compared with TPNCN-TPA; hence, the effective quasi-equivalent hybridization enhances OLED efficiency. The calculated LE % and CT % are displayed in Table S3 which shows HLCT, LE, and CT contributions to quasi-equivalent hybridization. The HLCT contribution is discussed from the electron−hole pair wave function (Figure S5—TPNCN-Cz; Figure S6—TPNCN-TPA) as well as the TDM (Figure 6—TPNCN-Cz; Figure S7—TPNCN-TPA): the diagonal part corresponds to LE which is situated on the main core, whereas the off-diagonal part corresponds to CT; excitation transferred the electron from the donor region to acceptor vicinity depending upon the electronic coupling which is investigated by distribution of electron density ($S_0$ to $S_{10}$ states). The new-

Figure 6. Computed contour plots of TDMs of TPNCN-Cz [S$_1$−S$_5$ states: density = transition = $n/I_{\text{Op}}(6/8 = 3)$].
born blue emitters show high quantum yield ($s/f$) of CNPIBP (0.85/0.76), NPIBN (0.75/0.68), CNPIBN (0.90/0.88), TPNCN-TPA (0.71/0.62), and TPNCN-Cz (0.78/0.72), and high fluorescence efficiencies are essential for efficient OLEDs (Table 1). The higher quantum yield is ascribed to the suppressed nonradiative emission because of molecular interactions, viz., intermolecular interaction between the cyano group and the phenanthrimidazole plane. Incorporation of cyanonaphthyl and biphenyl/binaphthyl into bulky phenanthrimidazole enhanced the intermolecular steric hindrance and forced the molecule to form a more twisted structure when packing in solid which results in less aggregation and lower quantum yield in the solid state. The harvested high $\phi$ and unchanged PL emission resulted from the various components and the CN group at a suitable position of D$_{-}\pi$A molecules is considered as a potential rare model in OLEDs.

2.7. Single-Carrier Devices. The charge injection as well as transport capacity of TPNCN-Cz, TPNCN-TPA, CNPIBN, 4,4′-bis(carbazol-9-yl)biphenyl (CBP):Ir(ppy)$_3$, TPNCN-TPA:Ir(ppy)$_3$, and TPNCN-Cz:Ir(ppy)$_3$, was investigated by fabrication of single-carrier devices [hole-only (h$^+$) and electron-only (e$^-$)]. Hole-only (h$^+$): (I) ITO/HATCN(8 nm)/CNPIBN/TPNCN-TPA/TPNCN-Cz (50 nm)/HATCN(8 nm)/LiF(1 nm)/Al(100 nm); (II) ITO/HATCN(8 nm)/TPNCN-TPA (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$/HATCN(8 nm)/LiF(1 nm)/Al(100 nm); (III) ITO/HATCN(8 nm)/CBP (30 nm): 5 wt % Ir(ppy)$_3$, or CBP (30 nm): 5 wt % Ir(ppy)$_3$/HATCN(8 nm)/LiF(1 nm)/Al(100 nm) and electron (e$^-$)-only; (IV) ITO/TPBi(8 nm)/CNPIBN/TPNCN-TPA/TPNCN-Cz (30 nm)/TPBi(8 nm)/LiF(1 nm)/Al(100 nm); (V) ITO/TPBi(8 nm)/TPNCN-TPA (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$/HATCN(8 nm)/LiF(1 nm)/Al(100 nm); (VI) ITO/TPBi(8 nm)/TPNCN-TPA (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$/HATCN(8 nm)/LiF(1 nm)/Al(100 nm) (Figure 7) devices were made. The current-density difference among single-carrier devices based on NPIBN, CNPIBP, CNPIBN, TPNCN-TPA, and TPNCN-Cz is very small relative to the CBP device. This shows that these bipolar materials effectively transport electrons as well as holes. A similar observation is made for TPNCN-TPA (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$/HATCN(8 nm)/LiF(1 nm)/Al(100 nm) (Figure 7). In the CBP: 5 wt % Ir(ppy)$_3$ device, the carrier current decreases significantly because the carrier may undergo deep trapping at the HOMO level of Ir(ppy)$_3$. However, in TPNCN-TPA (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$, or TPNCN-Cz (30 nm): 5 wt % Ir(ppy)$_3$/HATCN(8 nm)/LiF(1 nm)/Al(100 nm) device, the carrier current increased which may be attributed to the effect of direct injection into the dopant HOMO levels and the hopping transport through both TPNCN-Cz/TPNCN-TPA and dopant sites (Figure 7). The 8 nm TPBi in the electron-only device acts as a HBL (hole-blocking layer) to measure electron current only. The hole-current density in CNPIBP and CNPIBN was lower than that in NPIBN (Figure 7), which reveals that the CN group limits the h$^+$-injection as well as transportation to some extent. In CNPIBP and CNPIBN devices, a similar e$^-$-current charge was measured by high electric field and h$^+$-current was measured in low electric field. This shows that CNPIBP and CNPIBN materials may be used as a potential EML at low voltage for highly efficient OLEDs.
2.8. Electroluminescent Properties. The HOMO–LUMO energies of the molecules employed to fabricate the devices are presented in Figure 7. TADF materials show a flatdecay profile because of the slow TADF process in the conversion of the exciton to singlet state from the triplet state. However, the observed single-exponential sharp decay of
TPNCN-TPA and TPNCN-Cz shows that radiative excitions of TPNCN-Cz and TPNCN-TPA are short-lived without contribution by TADF (Figure 3). The mono exponential TRPL shows the existence of single emissive state, viz., HLCT. This is revealed by solventochromic studies in solvents of moderate polarity. This endorses the proposed molecular design (Scheme 1). Hence, high $\eta_s$ values observed in TPNCN-Cz and TPNCN-TPA are not due to the TTA or TADF mechanism.19

The blue device, ITO/NPB(60 nm)/NPIBN/CNPIBP/CBP:NPIBN/CBP:CNPIBP(20 nm)/TPBI-CNB(21%) and MCB (24%), and (iii) PPI-TPA-NzP (1.00 cd A−1),75 and (ii) PPI-pCN (54%). Thickness of LBPPP influences the $\eta_s$ (50 nm: 0.01 cd A−1; 40 nm—0.13 cd A−1; 30 nm: 0.40 cd A−1 and 20 nm: 0.68 cd A−1).19 The $\eta_s$ values obtained in the current study with 30 nm TPNCN-Cz (3.89 cd A−1) and 20 nm TPNCN-Cz (3.42 cd A−1) are larger than those reported already.87,88 For Cz-TPA device (3.89 cd A−1),75 and 0.77 lm W−1, respectively. The EL brightness of these compounds is linearly related to the current density. This indicates that TTA was insignificant.86 The wavelength of emission of TPNCN-Cz and TPNCN-Cz in the film are close to those dissolved in ether; this endorses the HLCT-emissive state. The $\eta_s$ and $\eta_x$ of the said devices and earlier reported70—85 devices are presented in Table S10. This reveals that the nondoped devices with NPIBN, CBP:CNPIBP, CBP:CNPIBP, and CBP: CNPIBP are the most efficient ones. These experimental results demonstrated that the additional triplet excitons have been utilized in the OLED applications for the HLCT character of TPNCN-TPA and TPNCN-Cz as presented in Scheme 1 and show the accuracy for our molecular design strategy. Devices with CNPIBP, NPIBN, CBP:CNPIBP, and CBP: CNPIBP, and CBP: NPIBN are the most efficient donors.

To enhance the efficiencies further, doped devices with NPIBN, CBP:CNPIBP, and CBP:CNPIBP as dopants were constructed with the structure of ITO/NPB(40 nm)/TCTA(5 nm)/CBP:NPIBN/CBP:CNPIBP/CBP:CNPIBP(20 nm)/TPBI-(50 nm)/LiF(1 nm)/Al(100 nm)); CBP [LUMO −2.7 eV; HOMO −6.1 eV] used as the host for the fluorescent dopants for its single high energy level. The doped device based on CBP: CNPIBN shows maximum efficiencies [\eta_s 5.4%; \eta_x 7.56 cd A−1; and \eta_\text{eff} 6.91 lm W−1] and CIE: (0.15, 0.09)] (Figure 8: Table 5). The PL and EL emissions of bis phenanthrimidazoles and D−π−A compounds are comparable with already reported best blue fluorescent OLEDs (Table S10).87 The high color purity and excellent luminescence make NPIBN, CBP:CNPIBP, and CBP:CNPIBP potential candidates in OLED lighting and full-color display.

Among the donor−π−acceptor compounds (TPNCN-Cz and TPNCN-TPA), the TPNCN-Cz device displays good performance. The $\eta_x \eta_\text{ee}$ and $\eta_\text{eff}$ are 4.00 cd A−1; 3.42 lm W−1, and 2.32%, respectively (Figure 8: Table 5). $\eta_\text{eff}$ is calculated from the following equation: EQE = $\eta_\text{out} \times \eta_\text{ee} \times \eta_\text{ee} \times \Phi_\text{PL}$ [\eta_\text{out}, coupling efficiency (20%); \eta_\text{ee} product of charge-recombination efficiency (100%); $\eta_\text{ee}$, radiative exciton production efficiency (25%); and $\Phi_\text{PL}$, PL quantum yield]. The $\eta_s$ for TPNCN-TPA and TPNCN-Cz based devices is calculated as 13−16% which indicates that γ < 100% because of very small unbalanced charge transportation.89 This result ascribed to the effective charge transportation to the EML by effective charge injection from the hole transport layer (HTL). The maximum $\eta_s$ is 16.3% for TPNCN-TPA and 16.1% for TPNCN-Cz, which is obtained from $\eta_s = \eta_\text{out} \times \eta_\text{PL} \times \eta_\text{ee} \times \eta_\text{ie}/\eta_\text{IR}$. The enhanced $\eta_\text{EQE}$ by 10.1% for TPNCN-TPA and by 11.6% for TPNCN-Cz as well as $\eta_s$ are probably because of retained CT % due to the CN group introduction in D−π−A compounds.

The efficiencies of the said devices and earlier reported70−85 devices are presented in Table S10. This reveals that the nondoped devices with NPIBN, CBP:CNPIBP, CBP:CNPIBP, and CBP: CNPIBP, and CBP: NPIBN are the most efficient donor. These experimental results demonstrated that the additional triplet excitons have been utilized in the OLED applications for the HLCT character of TPNCN-TPA and TPNCN-Cz as presented in Scheme 1 and show the accuracy for our molecular design strategy. Devices with CNPIBP, NPIBN, CBP:CNPIBP, and CBP: CNPIBP, and CBP: NPIBN are the most efficient ones. These experimental results demonstrated that the additional triplet excitons have been utilized in the OLED applications for the HLCT character of TPNCN-TPA and TPNCN-Cz as presented in Scheme 1 and show the accuracy for our molecular design strategy. Devices with CNPIBP, NPIBN, CBP:CNPIBP, and CBP: CNPIBP, and CBP: NPIBN are the most efficient ones. These experimental results demonstrated that the additional triplet excitons have been utilized in the OLED applications for the HLCT character of TPNCN-TPA and TPNCN-Cz as presented in Scheme 1 and show the accuracy for our molecular design strategy.
and Gao et al. observed 0.65 cd A\(^{-1}\) as \(\eta_c\) and 0.48 lm W\(^{-1}\) as \(\eta_p\) for Cz-phenanthrimidazole.\(^{88}\) These Cz compounds show lower efficiencies compared to TPNCN-Cz (4.0 cd A\(^{-1}\); 3.42 lm W\(^{-1}\)) and TPNCN-TPA (3.89 cd A\(^{-1}\); 3.15 lm W\(^{-1}\)). Modification of EML thickness is likely to enhance the efficiencies of the present materials. The device efficiency indicates that the synthesized materials are the best fluorescent OLEDs materials.

These TPNCN-TPA and TPNCN-Cz are employed as hosts for green and red phosphorescent dopants: green and red devices with configuration ITO/NPB(40 nm)/TCTA(5 nm)/TPNCN-Cz(30 nm): 5 wt % Ir(pppy)/TPNCN-TPA(30 nm): 5 wt % Ir(pppy)/TPBI(50 nm)/LiF(1 nm)/Al(100 nm); ITO/NPB(40 nm)/TCTA(5 nm)/TPNCN-Cz(30 nm): 8 wt % Ir(MQ)\(_2\)(acac)/TPNCN-TAPA(30 nm): 8 wt % Ir(MQ)\(_2\)(acac)/TPNCN-TPA(30 nm): 8 wt % Ir(MQ)\(_2\)(acac)/TPBI(50 nm)/LiF(1 nm)/Al(100 nm) (Figure 9) have been developed, and [Ir(pppy)\(_3\)]-ac-tris(2-phenylpyridine) iridium(III) and Ir(MQ)\(_2\)(acac)-bis(2-methylbenzol-[j,k] quinoxaline)acetylacetonate iridium(III) are used as EMLs for green and red devices, respectively. The device performances are presented in Figure 8. The EL and PL emission of doped films are similar (Figure S1). At 4% Ir(pppy)\(_3\) dopant concentration, two emission peaks are observed. In these devices, the TPNCN-Cz and TPNCN-TPA act as hosts for green phosphorescent dopant (Ir(pppy)\(_3\)) as well as blue emitters. A part of the formed excitons would transfer to triplet energy of Ir(pppy)\(_3\) to excite phosphorescence, whereas other parts of excitons would transfer to the ground state (\(S_0\)) to generate fluorescence.\(^{57}\) When the doping concentration increased to 5%, all generated excitons were transferred to Ir(pppy)\(_3\) to produce phosphorescent emission (Figure S1b). For the green device of TPNCN-Cz (30 nm): 5 wt % Ir(pppy)\(_3\), L is 8998 cd m\(^{-2}\); \(\eta_c\) is 38.4 cd A\(^{-1}\), and \(\eta_p\) is 34.6 lm W\(^{-1}\) at 2.7 V (Table S). The \(\eta_{ex}\) values of TPNCN-Cz:Ir(pppy)\(_3\) and TPNCN-TPA:Ir(pppy)\(_3\) are 19.7 and 19.6%, respectively. Similar to green devices, for a red device based on TPNCN-Cz:Ir(MQ)\(_2\)(acac), L is 39 926 cd m\(^{-2}\) with excellent efficiencies (\(\eta_{ex}\) 22.6%; \(\eta_c\) 26.1 cd A\(^{-1}\); and \(\eta_p\) 32.3 lm W\(^{-1}\) with CIE (0.64, 0.36) when compared with a TPNCN-TPA-based device (L—42 213 cd m\(^{-2}\); \(\eta_{ex}\) 20.3%; \(\eta_c\) 25.4 cd A\(^{-1}\); and \(\eta_p\) 30.8 lm W\(^{-1}\)) with CIE (0.64, 0.36). The above experimental results demonstrate that for green and red phosphorescent emission, TPNCN-TPA and TPNCN-Cz are efficient host materials (Table 5).

3. CONCLUSIONS

We have developed new blue emitters, bis phenanthroimidazole derivatives (NPB, CNPIBN, and CNPIBIn), and donor–spacer–acceptor compounds (TPNCN-TPA and TPNCN-Cz) with bipolar properties and superior thermal characteristics. For the fabricated CNPIBN device, \(\eta_{ex}\) is 4.96%; \(\eta_c\) is 7.46 cd A\(^{-1}\); and \(\eta_p\) is 6.85 lm W\(^{-1}\) at lower turn-on voltage. The doped one based on CBP: CNPIBN shows maximum efficiencies (\(\eta_{ex}\) 5.4%; \(\eta_c\) 7.56 cd A\(^{-1}\); and \(\eta_p\) 6.91 lm W\(^{-1}\)) and CIE: (0.15, 0.09). The nondoped TPNCN-Cz device shows maximum efficiencies (\(\eta_{ex}\) 2.32%; \(\eta_c\) 4.00 cd A\(^{-1}\); and \(\eta_p\) 3.42 lm W\(^{-1}\)) when compared to TPNCN-TPA (\(\eta_{ex}\) 2.01%; \(\eta_c\) 3.89 cd A\(^{-1}\); and \(\eta_p\) 3.15 lm W\(^{-1}\)). The TPNCN-TPA and TPNCN-Cz exhibit blue emission; CIE: (0.15, 0.10) and (0.15, 0.10). The increased \(\eta_c\) of 16.3% for TPNCN-TPA and 16.1% for TPNCN-Cz and increased \(\eta_{IQE}\) of 10.1% of TPNCN-TPA and 11.6% for TPNCN-Cz are probably due to the CT component from cyano substitution. The TPNCN-TPA and TPNCN-Cz are employed as the host for green and red phosphorescent devices, respectively. For the green device of TPNCN-Cz (30 nm): 5 wt% Ir(pppy)\(_3\), L is 8998 cd m\(^{-2}\); \(\eta_c\) is 28.4 cd A\(^{-1}\), and \(\eta_p\) is 34.6 lm W\(^{-1}\) at 2.7 V (Table S). The \(\eta_{ex}\) values of TPNCN-Cz:Ir(pppy)\(_3\) and TPNCN-TPA:Ir(pppy)\(_3\) are 19.7 and 19.6%, respectively. Similar to green devices, for the red device based on TPNCN-Cz:Ir(MQ)\(_2\)(acac), L is 39 926 cd m\(^{-2}\) with excellent efficiencies (\(\eta_{ex}\) 22.6%; \(\eta_c\) 26.1 cd A\(^{-1}\); and \(\eta_p\) 32.3 lm W\(^{-1}\) with CIE (0.64, 0.36) when compared with the TPNCN-TPA-based device (L—42 213 cd m\(^{-2}\); \(\eta_{ex}\) 20.3%; \(\eta_c\) 25.4 cd A\(^{-1}\); and \(\eta_p\) 30.8 lm W\(^{-1}\)) with CIE (0.64, 0.36). We have developed a chemical modification strategy to harvest high-performance full-color OLEDs by

![Figure 9. Energy-level diagram of green (a) and red (b) devices with molecular structures of functional materials used in devices.](image-url)
utilizing bis phenanthrimidazoles in doped and nondoped devices and bipolar luminescent materials having a D−π−A molecular structure.

4. EXPERIMENTAL SECTION

4.1. Measurements and General Methods. The 1H and 13C NMR were recorded using a Bruker 400 MHz spectrometer, and mass spectra were obtained from Agilent (LCMS VL SD). UV–vis absorption in solution and film was measured on a Lambda 35 PerkinElmer spectrophotometer with its integrated sphere (RSA-PE-20). PL spectra were recorded from an LSSS fluorescence spectrometer (PerkinElmer). TGA and DSC were performed with a thermal analysis system and NETZSCH-DSC-204 PerkinElmer, respectively, with a heating rate of 10 °C min−1 and a N2 flow rate of 100 mL min−1. Fluorescence lifetime of emissive materials was estimated from time-resolved fluorescence decay obtained by a TCSPC method (Horiba Fluorocube-01-NL lifetime system). The absolute quantum yield was determined using a cyclohexane solution and NETZSCH-DSC-204 PerkinElmer, and the purity of the emissive materials was analyzed by HPLC.

4.2. Computational Details. The ground (S0) state and excited (S1−S5) states of emissive materials were studied using Gaussian 09 program88 and a multifunctional wave-function analyzer (Multiwfn).89 The synthetic procedure is detailed in Scheme 2. The purity of the emissive materials was analyzed by HPLC.

4.3. 4-(2-(4-Bromophenyl)-1H-phenanthro[9,10-d]-imidazol-1-yl)naphthalene-1-carbonitrile (BPNICN). A mixture of 2.0 g 4-aminonaphthonitrile, 1.55 mmol) were refluxed with 4-aminonaphthonitrile (6 mmol) and ammonium acetate (61 mmol) in a minimum quantity of DMF was refluxed under N2 stream. A detailed synthetic route is presented in Scheme 2. mp 298 °C. Anal. Calcd for C30H16BrN3S: C, 76.48; H, 3.77; N, 7.96. 1H NMR (400 MHz, CDCl3): δ 7.39−7.53 (m, 6H), 7.65−7.89 (m, 9H), 8.12 (d, 2H), 8.89 (d, 2H). 13C NMR (100 MHz, CDCl3): 121.53, 122.65, 123.81, 125.19, 126.75, 127.63, 128.59, 129.86, 129.95, 130.57, 131.52, 132.57, 135.85, 136.82, 140.84. MALDI-TOF MS m/z: 547.86 [M+]. Calcd, 548.09.

4.6. 4,4′-Bis(1-(4-naphthyl)-1H-phenanthro[9,10-d]-imidazol-2-yl)binaphthalene (TPNPCN). 2.0 g of PPh3 (0.25 mmol) were refluxed with 7.5 mmol of 4-(diphenylamino)phenylboronic acid and 15 mL Na2CO3 in 20:15 mL toluene: ethanol. The TPA-TPNPCN obtained was subjected to device fabrication. Yield 61%. mp 298 °C. Anal. Calcd for C48H38N2S: C, 82.97; H, 4.35; N, 8.06. Found: C, 82.86; H, 4.28; N, 7.01. 1H NMR (400 MHz, CDCl3): δ 6.47−6.54 (m, 6H), 6.64 (t, 3H), 7.01 (d, 2H) 7.05−7.28 (m, 4H), 7.23−7.38 (m, 12H), 7.43−7.57 (m, 12H), 7.81−7.89 (m, 6H), 8.12−8.23 (m, 3H), 8.98 (d, 2H). 13C NMR (100 MHz, CDCl3): 109.43, 111.51, 114.89, 121.78, 122.54, 123.85, 126.67, 127.54, 128.65, 129.42, 131.26, 131.29, 132.51, 133.48, 136.65, 141.51, 146.48. MALDI-TOF MS m/z: 530.89 [M+]. Calcd, 531.02.

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4565 Article
Solvatochromism for HLCT character—Lippert–Mataga plot; absorption and emission spectra; EL spectra (inset: CIE coordinates); Lippert–Mataga plots 

AUTHOR INFORMATION

ASSOCIATED CONTENT

Supporting Information

S Supporting Information

Scheme of exciton decay process after hole and electron recombination; photophysical properties of TPNCN-Cz in different solvents; photophysical properties of TPNCN-TPA in different solvents; percentage transition of LE and CT of TPNCN-Cz and TPNCN-TPA; computed hole and electron overlap (S), distance between centroids of hole and electron (D, Å) and dipole moment (μ) for singlet states of TPNCN-Cz; computed hole and electron overlap (S), distance between centroids of hole and electron (D, Å) and dipole moment (μ) for singlet states of TPNCN-TPA; computed rmsd of electronic and hole, H index and t index singlet states of TPNCN-Cz; computed rmsd of electronic and hole, H index and t index singlet states of TPNCN-TPA; computed excitation energy (eV), excitation coefficient and Δr index (Å) for Singlet and triplet states of TPNCN-Cz; computed excitation energy (eV), excitation coefficient and Δr index (Å) for Singlet and triplet states of TPNCN-TPA; and comparison summary of device performances of blue OLEDs reported recently (PDF)
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