Efficient deep blue (CIE $\sim 0.08$) fluorophore-based benzimidazole with hybridized local and charge transfer (HLCT) excited state for OLEDs

Jaipal Devesing Girasea, Jairam Tagarea, Susmita Mukherjeeb, Tanwistha Chakrabratib, Ajay Perumalb and Sivakumar Vaidyanathan

$^a$Department of Chemistry, National Institute of Technology Rourkela, Rourkela, India; $^b$Department of Physical Sciences, Indian Institute of Science Education and Research (IISER), Functional NANO and Opto-electronics Lab (FNOL), Berhampur, Odisha, India

ABSTRACT

Development of efficient deep blue fluorophore with Commission Internationale de l'Eclairage (CIE) y value $<0.1$ is of great importance for display technology. Herein, we designed and synthesized a thermally stable deep blue emissive material 3-(2-(4'$''$-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1':4',1''':1',1''']terphenyl-4-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (MCNPIBI) by integrating moderate donor and acceptor, namely, phenanthroimidazole (PI) and benzimidazole with cyanophenyl (-CN) group at N1 position of the PI to tune the CT component in the excited states. The systematic theoretical and photophysical study reveals the MCNPIBI with hybridized local and charge transfer (HLCT) excited states. Time-dependent density functional theory (TD-DFT) calculation suggests that the reverse intersystem crossing (RISC) process in MCNPIBI occurs from high-lying triplet states to a singlet state. Furthermore, the synthesized deep blue emissive materials were employed as dopants in multilayer organic light emitting diode (OLED) devices, thus resulting in deep-blue electroluminescence (EL) with an emission wavelength of 447 nm and CIE coordinates of (0.15, 0.08), which are close to the standard values for blue emitters, as suggested by NTSC (0.14, 0.08). The OLED device displays a maximum current efficiency of 2.78 cd A$^{-1}$, a maximum power efficiency of 1.94 lm W$^{-1}$, and a maximum external quantum efficiency of 3.69%, respectively. In addition, the OLED device has a low turn in voltage of 3.8 V.

1. Introduction

The ever-increasing energy demand pushes the use of energy efficient smart displays and solid-state lighting technology. In this context, organic light emitting diodes (OLEDs) have gained much attention and showed striking benefits (high luminous efficiency, brightness, wide field-of-view and potential applications in comfortable and low-cost full color flat-panel displays) [1,2]. Among the three primary monochrome OLEDs, commercially relevant performance can easily be obtained from green and red emitters; however, achieving a display with pure deep blue emitters is still a challenging task [3–7]. Pure blue emitters have wide intrinsic band gaps that restrict high charge-injection barrier and unbalanced charge-injection and transportation in the device [8–11]. Even though the second and third generation OLEDs having emitters based on phosphorescent and thermally activated delayed fluorescence (TADF) concept showed extremely high external quantum efficiency (EQE) surpassing $\sim 30\%$ mostly using sky blue emitters [12], obtaining deep blue emitters with Commission Internationale de l’Eclairage (CIE) y value $<0.1$ matching with the prerequisite CIE coordinates defined by the National Television System Committee (NTSC)/European Broadcast Union (EBU) has been a real challenge [13–18]. Recently, TADF emitters having complicated molecular design strategy were used as blue emitters [19–22]. Unlike TADF and phosphorescent emitters, the synthesis of fluorescent-based deep blue emitters have a simple and straightforward design strategy [23,24]. In order to avoid concentration quenching and efficiency roll-off at a high current density (due to cumulative long-lived triplet dark excitons), the TADF and phosphorescent emitters are dispersed into a host matrix (having a high triplet state) [25]. An ideally ultra-stable and highly efficient fluorescent deep blue emitter does not need a host and is still...
seen as the most suitable in comparison to phosphorescent or TADF pure blue emitter in OLED devices [26]. To achieve this, certain features need to be fulfilled by the emitters that include appropriate spectral window with a CIEy value of < 0.1 (high color gamut), high PLQY, thermally stable, and optimistic energy levels to facilitate the charge injection in the device [27]. Particularly, designing a donor–acceptor (D – A) molecule with a hybridized local and charge transfer (HLCT) excited state is a very active strategy for high performance OLEDs. It is also worth noting that through a hot exciton channel (the component charge transfer [CT] excited state in the HLCT excited state), efficient reverse intersystem crossing (RISC) process by the small $\Delta E_{ST}$, leads to a high EUE. In addition, it shows short excited state lifetimes in comparison to TADF emitters. It is also documented that the emissive excited state is near a pure LE state rather than a CT state in weekly coupled HLCT blue emitters [28], which ultimately benefits the blue-shifted emission. Electron-donating/withdrawing strengths (moderate) of donor (D) and acceptor (A) of HLCT-based molecules play a vital role in regulating the energy of CT and LE state, resulting in an assured blue emission.

In this study, we designed and synthesized a new deep blue HLCT molecule (MCNPIBI), where phenanthroimidazole (PI) represents a highly efficient violet-blue chromophore with a moderate donor, while benzimidazole (BI) is a moderate acceptor with a propeller conformation. The diphenyl moiety acts as a conjugated core ($\pi$- spacer) connecting the BI, which can help in creating a charge-hopping channel that ultimately increases the electrical properties. Hence, the twisting D–$\pi$–A molecular conformation and the moderate electron donating and accepting ability can facilitate the partial separation of HOMO and LUMO, as well as the cyanophenyl group at the N1 position of phenanthroimidazole, thereby improving the CT component in the HLCT states of the molecule. The existence of the diphenyl moiety increases the conjugation length and advances the LE component. Simultaneously, the diphenyl moiety enhances twisting, which efficiently prevents the aggregation-induced quenching effect. MCNPIBI fluorophores were structurally characterized by spectroscopic technique, such as NMR spectroscopy and mass spectrometry. The electronic features were a priori understood by computational methods (DFT and TD-DFT). Theoretical and experimental investigations suggest that the MCNPIBI possesses an HLCT characteristic with RISC channels from the highest triplet level of MCNPIBI. The synthesized HLCT materials show deep blue emission with high photoluminescence quantum yield in both solution and thin film. The allowed electronic transition of MCNPIBI was realized from HOMO-LUMO+1. Encouraged by the theoretical and experimental results, we fabricated a multilayer OLED device. The OLED device shows a very low turn on voltage ($V_{on} = 3.8$ V) and deep blue EL with emission peaked at 447 nm with (0.15, 0.08) CIE coordinates, which are very close to the pure deep blue NTSC standard. The OLED device displays a maximum luminance of 6569 cd/m², a current efficiency of 2.78 cd A⁻¹, a maximum power efficiency of 1.94 lm W⁻¹, and a maximum external quantum efficiency of 3.69%, respectively.

2. Theoretical calculation

In order to understand the relationship between molecular structure properties and physical properties of the MCNPIBI, a computational investigation was carried out with the help of the density functional theory (DFT) by applying the B3LYP/6-31G (d, p) parameter, and the excited state energy level positions (singlet and triplet) were calculated by using time-dependent DFT (TD-DFT) [29]. The optimized geometry, frontier molecular orbitals, and electrostatic potential surface of MCNPIBI are schematically shown in Figure 1. After optimization, the molecular structure of MCNPIBI showed a highly twisted geometry, which could confine the intermolecular $\pi-\pi$ stacking and reduce the aggregation in solid states that usually results in either color impurities or reduction of emission in solid states [30,31]. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) energy levels, energy gaps ($E_g$), and excited energy levels (singlet and triplet) of MCNPIBI are tabulated in Table 1. The HOMO of the MCNPIBI was distributed on the phenanthroimidazole and $\pi$-linked aryl spacer, whereas the LUMO of MCNPIBI was mainly distributed on the N1-substituted cyanophenyl moiety. Based on Figure 1, it is clearly seen that the HOMO and LUMO are fully separated because of the strong electron withdrawing capability (as shown in Figure 1 the negative site is mainly localized on electron withdrawing (~ CN) moiety (red cloud on the electrostatic potential surfaces [EPS] map) of cyanide attached to the meta-position of N1-substituted phenyl ring. This automatically increases the CT characteristics of the excited states of MCNPIBI. However, the calculated HOMO to LUMO energy gap ($E_g$) for MCNPIBI is 3.38 eV, which ensures deep blue emission. Moreover, the LUMO+1 energy levels of MCNPIBI were distributed over the phenyl spacer and small contribution over PI and BI. The calculated energy gap between HOMO to LUMO+1 was 3.73 eV, as shown in Figure S15. The energy gap obtained from the HOMO to LUMO+1 in the MCNPIBI is in good alignment with the band gap obtained from the absorption spectra, thereby supporting the theorized separation of the electric and optical energy gaps. As a matter of fact, the transition from
the HOMO-LUMO was completely forbidden (results in lower $f = 0.025$) in the photoabsorption process due to complete separation. However, the transition from the HOMO-LUMO+1 in the MCNPIBI is allowed (results in higher $f = 1.645$) because of their effective overlaps in the Mos [32]. The calculated vertical excitation wavelengths, orbital contribution, and oscillator strength ($f$) of the fluorophores are listed in Table S3. Atom coordinates of all the synthesized fluorophores were given as supplementary (SI7).

To examine the excited state electronic transitions, oscillator strength and natural transition orbitals (NTOs) for the $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ ($n = 1–10$) were calculated by using TD-DFT [33]. The natural transition orbitals are evaluated with particle-hole pair contribution, as shown in Figure 2, and exhibited a hybrid splitting state character resulting from the coupling of LE and CT levels to form HLCT (Table 2). In regard to $S_0 \rightarrow S_1$ excitation, the “hole” was distributed on PI and small contribution on phenyl ring and “particle” were localizing on $\pi$-linked phenyl spacer and small fraction at five-membered PI rings. However, the transition direction of LE, CT, or HLCT in the case of MCNPIBI is found to be in phenyl spacer and towards BI means C2-substituted direction. The CT constituent is perpendicular to LE in the mix transition, thus forming hybrid HLCT states with lower oscillatory strength ($f_{S_0 \rightarrow S_4} = 0.0558$), as shown in Figure 2.

Additionally, the reverse intersystem crossing in the MCNPIBI energies of the first ten singlet and triplet excited states were calculated, and energy landscape is shown in Figure S16. The reverse intersystem crossing in MCNPIBI, CT states shown by $T_3$ energy levels tend to degenerate orbital coupling and lie close to $S_1 (\Delta E_{S_1 T_3} = 0.01 \text{eV})$. However, the energy difference between the $S_1$ and $T_1 (\Delta E_{S_1 T_1} \sim 0.3 \text{eV})$ of MCNPIBI indicates that the RISC from $T_1 \rightarrow S_1$ is not expected to occur.

3. Synthesis and characterization

The synthesized blue-emitting fluorophore MCNPIBI employs imidazole derivatives as a mild electron donor (D) and a mild acceptor (A), i.e. D phenanthroimidazole (PI) having cyanophenyl substituent at N1-position and A benzimidazole (BI), respectively. The synthetic route is shown in Scheme 1 [34,35]. BBI-Br, Intermediates-I, Figure S1 were synthesized by using condensation reaction, and $4^\prime$-bromo- [1,10-biphenyl]-4-carbaldehyde and Intermediates-II Figure S1, as well as final fluorophores, were synthesized by using Suzuki coupling reactions.

4. Synthesis of 3-(2-(4$^\prime$-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1$^\prime$;4,1$^\prime$-terphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (MCNPIBI)

Meanwhile, 20 mL toluene, 10 mL ethanol, and 8 mL 2 M Na$_2$CO$_3$ aq. were added to a mixture of 0.482 g 2-($4^\prime$-bromo-[1,1$^\prime$-biphenyl]-4-yl)-1-phenyl-1H-benzo[d] imidazole (BBI-Br, 0.96 mmol), 0.500 g 3-($2^\prime$-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-phen-
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Figure 2. Natural transition orbital pairs with (HONTOs and LUNTOs) transition character analysis for singlet states ($S_1$–$S_{10}$) of MCNPIBI [f-oscillator strength and % weights of hole-particle].

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 MCNPIBI from NTOs.

| Energy level | $E_S$ (eV) | Oscillator Strength (f) | $\mu$ (D) | NTO Transitions | $E_T$ (eV) | $\Delta E_{ST}$ (eV) | NTO Transitions |
|--------------|-----------|------------------------|----------|-----------------|-----------|---------------------|----------------|
| 1            | 3.38      | 0.9249                 | 3.38     | 135$^{\text{100\%}}$–136 | 0.67      | 2.71                | 136$^{\text{98\%}}$–137 |
| 2            | 3.63      | 0.0916                 | 1.13     | 135$^{\text{28\%}}$–141 | 1.77      | 1.86                | 133$^{\text{10\%}}$–141 |
| 3            | 3.69      | 0.9477                 | 1.59     | 134$^{\text{32\%}}$–136 | 1.80      | 1.89                | 134$^{\text{13\%}}$–136 |
| 4            | 3.90      | 0.0558                 | 0.78     | 131$^{\text{27\%}}$–138 | 2.80      | 1.10                | 135$^{\text{13\%}}$–138 |
| 5            | 3.94      | 0.1768                 | 2.34     | 134$^{\text{31\%}}$–137 | 2.08      | 1.86                | 126$^{\text{13\%}}$–144 |
| 6            | 4.05      | 0.0226                 | 0.31     | 133$^{\text{37\%}}$–137 | 2.16      | 1.89                | 130$^{\text{33\%}}$–135 |
| 7            | 4.12      | 0.0089                 | 1.37     | 134$^{\text{28\%}}$–136 | 2.25      | 1.87                | 128$^{\text{12\%}}$–135 |
| 8            | 4.19      | 0.0277                 | 0.35     | 135$^{\text{19\%}}$–141 | 2.33      | 1.84                | 119$^{\text{14\%}}$–135 |
| 9            | 4.46      | 0.0064                 | 1.53     | 133$^{\text{27\%}}$–136 | 2.53      | 1.73                | 130$^{\text{16\%}}$–135 |
| 10           | 4.26      | 0.0019                 | 1.05     | 131$^{\text{22\%}}$–136 | 2.53      | 1.73                | 130$^{\text{18\%}}$–137 |

anthro[9,10-d]imidazol-1-yl)benzonitrile (m-CNPIPin) (0.96 mmol) and 55.44 mg Pd(PPh$_3$)$_4$ (0.048 mmol). Then, the suspension was heated at 90°C with stirring under nitrogen atmosphere. After 24 h, the mixture was allowed to cool to room temperature, extracted with CH$_2$Cl$_2$, and dried over anhydrous MgSO$_4$ before removing the solvent. Finally, the raw product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as eluent to give as a yellow solid (73.5%) $^1$H NMR (400 MHz CDCl$_3$, TMS, δ ppm) 8.87 (d, $J$ = 8.1 Hz, 1 H), 8.79 (d, $J$ = 8.2 Hz, 1 H), 8.72 (d, $J$ = 8.2 Hz, 1 H), 7.92 (dd, $J$ = 17.1, 7.8 Hz, 2 H), 7.84 (d, $J$ = 2.1 Hz, 1 H), 7.82–7.73 (m, 3 H), 7.72–7.62 (m, 7 H), 7.57 (td, $J$ = 8.7, 3.5 Hz, 6 H), 7.53–7.50 (m, 2 H), 7.46 (dd, $J$ = 10.7, 7.6 Hz, 1 H), 7.39–7.30 (m, 3 H), and 7.29–7.21 (m, 4 H), 7.06 (d, $J$ = 8.1 Hz, 1 H);
Scheme 1. Synthetic routes and molecular structure of MCNPIBI.

13C NMR (100 MHz, CDCl3, TMS, δ ppm) 152.0, 150.6, 143.0, 133.9, 133.5, 132.6, 131.2, 130.0, 129.5, 128.7, 127.5, 127.4, 127.0, 126.8, 126.8, 126.6, 126.0, 125.3, 124.5, 123.4, 123.2, 123.1, 122.9, 120.3, 119.9, and 110.47. MALDI-TOF (m/z): [M + H]: 740.57 is calculated for C53H33N5: 740.28.

5. Results and discussions

5.1. Thermogravimetric analysis

Thermal stability is an important parameter for the fabrication of organic-light-emitting devices (vacuum-evaporated OLEDs). Therefore, to realize the thermal stability of the synthesized blue emissive materials, thermogravimetric analysis (TGA) was performed in the range of 25°C to 700°C under nitrogen atmosphere. TGA curves of MCNPIBI were shown in Figure 3 and the corresponding data were listed in Table 4. Figure 3 shows that the MCNPIBI fluorophore holds excellent thermal stability with thermal decomposition temperature (T_d) (5% weight loss of initial weight) of around 412°C. The high temperature attributed to the rigid and bulky skeleton of PI and BI units. The excellent thermal performance offers potential thermal stability for organic electroluminescent devices [36].

Figure 3. Thermogravimetric curves of MCNPIBI (at a scan rate of 10°C/min).
Section 5.2. Electrochemical properties

In order to examine the electrochemical behavior and determine the exact energy levels (HOMO-LOMO) of MCNPIBI, cyclic voltammetry (CV) was conducted in a solution (10^{-5} M in DMF). Figure 4 displays the cyclic voltammogram of MCNPIBI, and corresponding electrochemical data were presented in Table 3. Based on Figure 4, it was found that the MCNPIBI possesses a distinct redox behavior, which indicates fluorophore bipolar charge transporting capabilities. In agreement with the onset potentials, the HOMO and LUMO energy levels were calculated by using Equations (1) and (2) [37].

\[
E_{\text{HOMO}} = - (E_{\text{onset}}^{\text{ox}} + 4.4) \text{eV} \quad (1)
\]

\[
E_{\text{LUMO}} = - (E_{\text{onset}}^{\text{red}} + 4.4) \text{eV} \quad (2)
\]

The energy level of HOMO was calculated and found to be -5.93 eV and the energy level of LUMO was found to be -2.47 eV, with the energy difference between HOMO and LUMO (electrochemical band gap) of 3.46 eV.

Section 5.3. Optical properties

The photophysical properties of the synthesized blue emissive material were investigated by using the UV-Vis absorption and photoluminescence (PL) spectroscopy. The UV-Vis absorption spectra in the THF, as well as the spin-coated neat thin film and PL spectra in the THF, spin-coated neat film and solid, were shown in Figure 5, and the details of photophysical data were tabulated in Table 4. The THF solvent MCNPIBI shows two distinct absorption bands, as shown in Figure 5(a). The lower wavelength strong absorption band at \(\sim 259\) nm corresponds to the \(\pi-\pi^*\) transitions of aromatic phenyl rings [38-40], while a lower energy and wide absorption peaks at \(\sim 344\) nm and a small shoulder peak at \(\sim 364\) nm, which might be observed due to the \(\pi-\pi^*\) transitions, as well as intramolecular charge transfer between phenanthroimidazole (PI) and benzimidazole moiety (BI) moiety [41]. However, in a neat thin film, the absorption spectrum of the fluorophore was found to be broad and occurs at \(\sim 301\) nm with a shoulder peak at \(\sim 379\) nm that is slightly red shifted than that of the solution state. This may be due to its relative \(\pi-\pi\) stacking interactions, as shown in Figure 5(b) [42]. Diffuse reflectance spectra shown in Figure 6(b) (using neat thin film) of MCNPIBI were executed in order to evaluate the optical band gap by employing the Kubelka-Munk function [43] and the resulting optical band gap was found to be 3.73 eV, thereby indicating that MCNPIBI has the potential to realize deep blue emission, as displayed in Table 3. In addition, it is observed that the obtained band gap from the DRS of MCNPIBI matches with the theoretically calculated band gap. The PL spectra of MCNPIBI in dilute solution is shown in Figure 5(a), and the neat thin film and solid are shown in Figure 5(b). The resultant PL data are tabulated in Table 4. Based on Figure 5(a), it turns out that MCNPIBI shows a strong emission in the deep blue region with an emission maxima of 427 nm.

However, the emission maxima of MCNPIBI in the neat thin film appeared at 451 nm, which showed a 23 nm red shift compared to the solution, and in solid-state emission maxima at 469 nm, it showed a 42 nm red shift compared to the solution. This may be due to the intermolecular interaction in the solid states [44]. The CIE color chromaticity of MCNPIBI was observed in the deep blue region, as shown in the Figure S13 and the corresponding CIE color coordinates (x and y) tabulated in Table S1. The absolute photoluminescence quantum yield (\(\Phi\)) was also calculated in the solution, as well as in the neat thin film. MCNPIBI shows good quantum yield in the solution, as well as in the thin film of 57% and 36%, respectively (Table 4).

To further investigate the excited state properties of MCNPIBI, fluorescence lifetime (10^{-5} M in CHCl_3) in the solution were measured by using the time-correlated single photon counting (TCSPC) technique. The lifetime decay of MCNPIBI was shown in Figure 6(a). The fluorescence lifetime of the MCNPIBI was found to be 1.65 ns (Table S2). The one lifetime decay profile indicates that it may have LE and CT states in the S_1 state that are highly mixed or hybridized, thereby indicating HLCT in the S_1 state of all the molecules [45].
Table 3. Electrochemical properties of MCNPIBI.

| Fluorophore | $E^0_\text{ox}$ (V) | $E^0_\text{red}$ (V) | HOMO (eV) | LUMO (eV) | $E^0_\text{g}$ (eV) | $E^0_\text{T}$ (eV) |
|-------------|------------------|------------------|-----------|-----------|----------------|----------------|
| MCNPIBI     | 1.53             | −1.93            | −5.93     | −2.47     | 3.46           | 3.73           |

a) Onset oxidation potential; b) Onset reduction potential; c) Electrochemical band gap determined from cyclic voltammetry; and d) Optical band gap estimated from reflectance spectra.

Figure 5. Normalized UV-vis absorption spectra and PL spectra in a) THF solution ($10^{-5}$ M), and b) Normalized UV-vis absorption spectra of neat film and PL spectra of the neat film and solid of MCNPIBI.

5.4. Solvatochromism

To further study the influence of solvents on the excited states of the properties of MCNPIBI, Solvatochromism study was carried out in different solvents with increasing polarity (from low polar hexane to more polar DMSO solvents), as displayed in Figure 7(a). Figure 7(a) shows that there is no significant change in the absorption spectra of MCNPIBI in different solvents, thereby indicating that the ground state is not an effect of solvents on the UV-Vis absorbance spectra. Meanwhile, PL emissions have shown a gradual bathochromic shift from low polarity to high polarity solvents, thereby indicating ICT characteristics. PL emissions of MCNPIBI observed a red shift of 50 nm from 401 nm in non-polar hexane to 451 nm in polar DMSO, respectively. With increasing polarity, full width at half maximum (FWHM) also increases with broadening in the PL emission peaks, clearly indicating CT in excited states of all fluorophores [46]. The detailed photophysical data were tabulated in Table 5. Additionally, it is observed that the PL emission spectra in hexane and toluene show two fine vibrational structure spectra, which reveal a locally excited (LE) feature of excited state in the non-polar solvent. With increasing polarity after toluene, the emission peak becomes non-vibrational and remains so until DMSO is used, which also indicates CT in excited states [47]. This outcome may indicate that the LE and CT states are lying close, so a slight change in the solvent polarity CT character dominates in excited states [48].

In order to study the influence of solvent environment to the photophysical properties of fluorophore, the Lippert-Mataga equation can also be used, which thoroughly debated the interactions between the solvent and the dipole moment of the solute in the ground state ($S_0$) and the lowest excited states ($S_1$). Equations (3) and (4) of Lippert-Mataga set out the Stokes shift (cm$^{-1}$) as a function of change in dipole moment ($\Delta \mu_{ge} = \mu_e - \mu_g$) [49,50].

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3}f(\varepsilon, n)$$ (3)

Table 4. Key photophysical properties of all synthesized fluorophores.

| Fluorophore | $T_d^\circ$C | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\Phi_1$ % | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\Phi_1$ % | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | $S_1$ (eV) | $T_1$ (eV) |
|-------------|-------------|----------------------|---------------------|------------|----------------------|---------------------|------------|----------------------|---------------------|-----------|-----------|
| MCNPIBI     | 412         | 259, 344, 364         | 427                 | 56         | 301, 379             | 451                 | 36         | 391                  | 469                  | 3.17      | 3.05      |

$^a$Thermal decomposition temperature corresponding to 5% weight loss. $\lambda_{abs}$ = absorption maximum, $\lambda_{em}$ = emission maximum, $\lambda_{ex}$ = excitation maximum, $\Phi_1$ = absolute fluorescence quantum yield in CHCl$_3$ ($10^{-3}$ M), $\Phi_1$ = absolute fluorescence quantum yield in thin film, $^b$singlet energy obtained from the onset emission PL spectra, and $^c$triplet energy obtained from the 77 K PL spectra.
Figure 6. (a) Time-resolved PL (TCSPC) in CHCl₃ solution, and (b) diffuse reflectance spectra of the molecule of MCNPIBI.

Figure 7. Normalized UV-Vis absorbance/PL spectra and the Lippert-Mataga model in various solvents for MCNPIBI.

Table 5. Key photophysical properties of MCNPIBI.

| Solvents | Δf  | λ₂₂₃ (nm) | λ₂₃₆ (nm) | Stokes shift (cm⁻¹) | FWHM (nm) |
|----------|-----|-----------|-----------|---------------------|-----------|
| Hexane   | 0.0012 | 340       | 401       | 4480                | 57        |
| Toluene  | 0.0131 | 347       | 412       | 4540                | 58        |
| THF      | 0.210  | 343       | 427       | 5740                | 68        |
| ACN      | 0.305  | 336       | 442       | 7140                | 81        |
| DMF      | 0.276  | 338       | 443       | 7010                | 82        |
| DMSO     | 0.263  | 342       | 451       | 7060                | 85        |

where (ν₀ - νᵣ) is the Stokes shift (cm⁻¹) between the absorption and fluorescence emission maxima [ν₀ = 1/λ₂₂₃ (max), νᵣ = 1/λ₂₃₆ (max)], h is Planck’s constant, c is velocity of light, μₑ and μᵣ are the dipole moment in excited states and ground states, respectively.

\[ Δf = f(ε, n) = \frac{ε - 1}{2ε + 1} - \frac{n^2 - 1}{2n^2 + 1} \]

\[ a = \left( \frac{3M}{4Nπd} \right)^{\frac{1}{3}} \]

where Δf is the orientation polarizability of solvents, α is the solvent cavity radius derived from the Avogadro’s number (N), molecular weight (M), and the density (d = 1.0 g/cm³); and ε, and n are the solvent dielectric and solvent refractive indices, respectively. The plot was drawn from Stokes shift as a function of orientation polarizability (Δf) [51,52]. Figure 7(b) shows the linear relationship of Stokes shift and orientation polarizability of MCNPIBI in different solvents, and corresponding data are summarized in Table 5. Based on Figure 7(b), correlation coefficient (R²), slope, and intercept noted for MCNPIBI are R² = 0.9357, slope = 9033 cm⁻¹, and intercept = 4386 cm⁻¹, respectively.

5.5. Electroluminescence properties

Doped blue OLED device was fabricated and characterized with MCNPIBI emitter molecule. We fabricated a multilayer OLED device with a device configuration of glass substrate on which indium-tin-oxide (ITO) was
prepatterned with 1 nm of MoO₃, 35 nm of 4,4’-bis(9H-carbazol-9-yl)biphenyl (CBP), 3 nm of MoO₃, an emission layer (15 nm) consisting of CBP with MCNPIBI as dopant emitter in a host-guest design with 10 wt% of the guest molecules, 65 nm thick 1,3,5-tri(1-phenyl-1H-benzo[d]-imidazol-2-yl)phenyl (TPBi) electron transport layer (ETL), 1 nm thick lithium fluoride (LiF), and 100 nm of aluminium (Al) metal cathode sequentially deposited, as shown in Figure 8.

The electroluminescence (EL) spectra of the OLED device measured the overlap with the photoluminescence (PL) spectra of MCNPIBI thin films, thereby suggesting that the EL originates from the MCNPIBI molecule. The emission spectrum resembles the PL emission spectra of the vacuum-deposited films, thereby indicating good exciton confinement in the emission layers and electroluminescence due to MCNPIBI molecules, as shown in Figure 9.

The CIE coordinates remain stable at (x, y) extracted from the voltage dependent spectra, as shown in Figure S17. Figure 10 shows current-voltage-luminance (J-V-L)
characteristics of the OLED device. The blue-emitting OLED device has a low turn on voltage of 3.8 V and a maximum luminance of 6000 cd m⁻² that can be achieved at a voltage of 14 V as displayed in Table 6. The display relevant 100 cd/m² can be achieved at a voltage of 6.5 V. The HOMO and LUMO levels of MCNPIBI were measured via CV and absorption spectroscopy. In addition, the HOMO and LUMO levels of MCNPIBI were measured from CV and the values were found to be −5.93 and −2.47 eV, respectively. CBP has HOMO and LUMO of −6.0 and −2.9 eV, respectively, and a triplet energy of 2.5 eV. The current efficiency and external quantum efficiency (EQE) of OLED devices are shown in Figure 11. The OLED device displays a maximum luminance of 6,569 cd/m², a current efficiency of 2.78 cd A⁻¹, a maximum power efficiency of 1.94 lm W⁻¹, and a maximum external quantum efficiency of 3.69%.

6. Conclusion

In summary, a thermally stable moderate donor and moderate acceptor (D-π-A) type efficient deep blue emitter (MCNPIBI) using phenanthroimidazole and benzimidazole has been successfully designed and synthesized. The theoretical and photophysical properties manifest an emitter with HLCT excited states. The synthesized emitter shows deep blue emission in the solution, as well in the solid states with high PLQY in solution and in thin film. The resultant emitter can be used as dopants in a multilayer OLED device. The doped device of MCNPIBI shows deep blue EL with an emission peak of 447 nm and CIE coordinates of (0.15, 0.08), which are very close to the NTSC standard blue CIE coordinates (0.14, 0.08). The doped device exhibits an EQE max of 3.69%, a PEmax 2.78 cd A⁻¹, and a CE max of 1.94 lm W⁻¹, with a maximum luminance of 6,569 cd m⁻². The EL characteristics of the MCNPIBI reveal its potential as efficient deep blue emitters for display application.

Supporting information

Supporting information includes NMR spectra (¹H and ¹³C), mass spectra of the compounds, CIE coordinates for the compounds in solutions, thin film and solid phase, vertical transition, and atom coordinates of all the fluorophores.

Table 6. EL performance of blue OLEDs based on MCNPIBI emitters.

| Emitter | λ max (nm) | O. V. (V) | PE100/CE100/ EQE100 (lmW⁻¹ cdA⁻¹/%) | PE1,000/CE1,000/ EQE1,000 (lmW⁻¹ cdA⁻¹/%) | PE max/ CE max/ EQE max (lmW⁻¹ cdA⁻¹/%) | CIE coordinates | L max (cdm⁻²) |
|---------|------------|----------|------------------------------------|---------------------------------|-----------------------------------|----------------|-------------|
| MCNPIBI | 441        | 3.8      | 1.0/1.9/2.8                        | 0.5/1.6/2.4                    | 1.94/2.78/3.69                    | (0.15, 0.08)  | 6,569       |

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Disclosure statement

No potential conflict of interest was reported by the author(s).

Notes on contributors

Jaipal Devesing Girase received his Bachelor of Science (BSc) and Master of Science (MSc) from the Department of Chemical Sciences North Maharashtra University, Jalgaon in 2015 and 2017, respectively. He is currently a PhD candidate under the guidance of Dr. Sivakumar Vaidyanathan in the Department of Chemistry at the National Institute of Technology Rourkela, India. At NIT Rourkela, his research focuses on the design and synthesis of blue organic light emitting materials and their applications in OLEDs.

Dr. Jairam Tagare received his Bachelor’s of Science (BSc 2007) from Kakatiya University and Master’s of Science (MSc 2010) from Andhra University. He received his PhD in Material Chemistry (Design and synthesis of organic molecules) (2020) from National Institute of Technology Rourkela, Rourkela, under Prof. Sivakumar Vaidyanathan, in the Department of Chemistry. His main research focuses on the design and synthesis of small molecule-based blue organic materials, their experimental and theoretical study, and their OLEDs applications.

Susmita Mukherjee received her Bachelor of Science (BSc) and Master of Science (MSc) degrees from Vidyasagar College for Women (Affiliated to Calcutta University) and The University of Burdwan in 2016 and 2018, respectively. Since 2018, she has been pursuing doctoral studies (PhD) in the Indian Institute of Science Education and Research, Berhampur (IISER-Berhampur), Odisha, India under the guidance of Dr. Ajay Perumal in the Department of Physical Sciences. Her current research interest is focused on light-emitting devices based on organic and lead halide perovskite semiconductors.
Tanwistha Chakrabarti received her Bachelor’s degree (2015) and Master’s degree (2017) in Physics from the University of Calcutta and Presidency University, respectively. She joined the Indian Institute of Science Education and Research, Berhampur (IISER-Berhampur), Odisha, India in 2018 to pursue her doctoral studies (PhD) as an INSPIRE (DST) fellow under the supervision of Dr. Ajay Perumal in the Department of Physical Sciences. Her current research interest is focused on organic-inorganic hybrid lead halide perovskite solar cells.

Dr. Ajay Perumal is an Assistant Professor at the Department of Physics in the Indian Institute of Science Education and Research, Berhampur (IISER-Berhampur), Odisha, India. He obtained his MSc from the University of Stuttgart/ Max Planck Stuttgart, Germany (2007). He pursued his PhD at the Technical University of Dresden under the guidance of Prof Karl Leo (2012). He went on to do postdoctoral work in the Imperial College London, UK (2012–2015) and NTU Singapore (2016–2017). His primary research interests are light-emitting devices and photovoltaics/solar cells with soft semiconductors.

Sivakumar Vaidyanathan received his Bachelor’s degree (2000) and Master’s degree (2002) in Chemistry from the Muthurangam Government Arts College, Vellore (affiliated to the University of Madras) and his PhD in Solid-State Chemistry (2007) from the Indian Institute of Technology, Madras, with Prof. U. V. Varadaraju. Then, he moved to Prof. Duk Young Jeon’s group at the Korea Advanced Institute of Science and Technology, Republic of Korea as a Brain Korea 21 postdoctoral research fellow (2007–2009). He also worked as a postdoctoral fellow at the Commissariat à l’Énergie Atomique (CEA), Saclay, France for a year. After spending a year in NIT Calicut as a faculty member in the Department of Chemistry, he moved to the Department of Chemistry at the National Institute of Technology Rourkela. His research focuses on lanthanide photochemistry and photophysics, molecular materials (including deep blue) for OLEDs, phosphors for LEDs (solid-state lighting), and organic fluorophores for diverse applications.

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