Mild donor–π–mild acceptor (mD–π–mA) benzimidazole-based deep blue fluorophores with hybridized local and charge transfer (HLCT) excited states for OLEDs

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ABSTRACT
The design of an efficient pure blue emitter to achieve stable, long operating organic light-emitting diode (OLED) devices still poses a significant challenge. Although through phosphorescence and thermally activated delayed fluorescence concepts, efficient and stable monochrome green and red OLEDs can be realized, the design of stable and efficient blue emitter has been a significant challenge. All efforts so far have resulted in severe efficiency roll-off and limited device lifetime. Therefore, developing efficient blue-emitting fluorescence materials with little or no efficiency roll-off is of great importance for commercial display OLEDs. In this context, we have designed and synthesized two pure blue fluorescence light-emitting materials that are thermally stable and have improved photophysical properties: 2-(4′′-(1-(4-(tert-butyl)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)-[1,1′:4,1′′:4′′′,1′′′]-terphenyl)-4-yl)-1-phenyl-1H-benzo[d]imidazole (PTBIBI) and 2-(4′′-(4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazol-2-yl)-[1,1′:4,1′′:4′′′,1′′′]-terphenyl)-4-yl)-1-phenyl-1H-benzo[d]imidazole (MCFBIBI). These emitters possess a hybrid local and charge-transfer (HLCT) state and have high photoluminescence quantum yields (>90%). The doped devices based on PTBIBI display a reasonably good device performance with the Commission International de l’Eclairage (CIE) coordinates of (0.15, 0.06) in the deep blue region and g maximum luminance of 6559 cd m−2 at a very low turn-on voltage (3.2 V) corresponding to the bandgap value of the blue emitter.

1. Introduction
Pure blue organic emitters for blue organic light-emitting diodes (OLEDs) have attracted enormous interest because of their importance in future generation flat panel displays and solid-state lighting applications, as all primary colors are equally important to generate full colors OLED displays. To date, red and green emitters having high efficiency and long lifetime have been widely reported [1–3]. However, the performance of blue emitter lags behind significantly when compared to other primary (red and green) color emitters in terms of stability and lifetime. Blue emitters also carry limited delocalization that affects the electron injection and device efficiency due to their intrinsic wide energy gap, which causes unbalanced charge injection as well as hindered charge transport [4–6]. Therefore, the development of a highly efficient deep-blue emitter remains an important and crucial research theme. In addition, the CIE coordinates required for blue OLEDs according to the National Television System Committee (NTSC) and European Broadcasting Union (EBU) are stringent, with blue CIE coordinates of (0.14, 0.08) and (0.15, 0.06) required for NTSC and EBU, respectively. Much of the efficient blue OLED emitters reported are in the sky blue region and do not satisfy these requirements. Consequently, for excellent multi-color display, blue fluorophores material showing CIE coordinates with y < 0.1 are in high demand [7–10]. The first generation emitters have internal quantum efficiency (IQE) limited to 25%, as 75% of triplet excitons are lost due to quantum mechanically forbidden triplet singlet transition in pure organic emitters [11–14]. To achieve 100% IQE, phosphorescent OLEDs (second generation) containing heavy metals such as platinum (Pt) and Iridium (Ir) with significant spin mixing due to...
heavy metal presence overcomes the issue of forbidden transition and utilizes both the singlet and triplet channel [15–17]. However, achieving deep blue emission in these materials has been hindered because these emitters suffer from significant material instability attributed to their large bandgap. Moreover, deep-blue OLEDs with phosphorescent emitters suffer from device lifetime and significant efficiency roll-off [18–20]. More recently, thermally activated delayed fluorescence (TADF) emitters, which realize IQE of 100% by harvesting 75% triplet excitons using reverse intersystem crossing (RISC) from triplet excited state \( T_1 \) to singlet excited state \( S_1 \), have been widely reported as alternatives for deep blue emission. Although the TADF emitters offer advantages such as efficiency and metal-free emitters, the synthesis of deep-blue TADF emitters remains a tedious task since it requires a small \( (\Delta E_{ST} < 0.05 \text{ eV}) \) energy difference between \( S_1 \) and \( T_1 \) energy level \( (\Delta E_{ST}) \) for efficient RISC process. To achieve small \( \Delta E_{ST} \), the spatially separated frontier molecular orbitals and molecular design strategy involving the engineering of molecules with twisted electron donor–acceptor (D-A) structure is employed. This strategy is synthetically challenging in terms of achieving deep blue emission with D-A type molecules because there is strong intramolecular charge transfer as well as various transition states, usually resulting in red-shifted emission. The TADF OLEDs that are currently reported have poor device lifetime and large efficiency roll-off because the annihilation of triplet excitons is severe due to delay in RISC from triplet to singlet channel, especially at high current and exciton densities [21–24].

Ma et al. proposed a new mechanism that breaks the 25% higher limit of singlet exciton proportion in OLEDs, in which excited states are presented as HLCT states with noticeably intercrossed locally emissive and CT character components [25, 26]. Therefore, the HLCT state has attracted growing attention since it can achieve high theoretical exciton utilization efficiency (EUE) through fast RISC from high-lying triplet states \( T_m \) \((m \geq 2)\) called hot exciton to \( S_1 \) and the mechanism called hot exciton mechanism (Figure 1). The rapid high-lying RISC can efficiently decrease triplet exciton concentration when current density increases and consequently ensure less efficient roll-off. However, molecular design plays an important role in achieving an HLCT state. The molecular structure possesses the balanced intramolecular charge transfer (CT) and locally excited (LE) state by avoiding strong donor and acceptor moiety. To date, numerous efforts have been devoted to developing deep blue emissive materials based on the donor–acceptor (D-A) and donor-\( \pi \)-acceptor (D-\( \pi \)-A) design strategy with different donor and acceptor units [27, 28]. Among them, benzimidazole [29–31] is gaining much attention in the field of organic electronics because of its easy synthesis procedure, satisfactory thermal stability, and ability to give a very narrow emission band (less full width at half maximum (FWHM)). This is attributed to the great twisting conformation of imidazole unit as well as benzimidazole’s amphoteric nature, with one nitrogen being electron-rich and another being electron-deficient. Consequently, it will show donor properties when attached to the electron-withdrawing group and vice-versa [32]. Hence, in the present investigation two different imidazoles, mild donor (benzimidazole) and mild acceptor (benzimidazole) (D-\( \pi \)-A) \( 2\-(4''\-(1-(4-(tert-butyl)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)-1′,1′′-terphenyl)-4-yl)-1-phenyl-1H-benzo[d]imidazole \( \text{(PTBIBI)} \) and 2-(4''''-(4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazol-2-yl)-1′,1′′-terphenyl)-4-yl)-1-phenyl-1H-benzo[d]imidazole \( \text{(MCFBIBI)} \) are designed. They are synthesized with hybridized local and charge-transfer (HLCT) excited states and different substituent at the N1 position of imidazole as the N1 position enhances the orbital coupling and tune molecular excited states properties (Scheme 1). The PTBIBI and MCFBIBI emitters show deep blue emission in solution as well as solid states with CIEY of 0.06 with high photoluminescence quantum yield (PLQY). Cyclic voltammetry and DFT calculations reveal that materials possess bipolar charge transport properties. In addition, we have fabricated OLED devices with both these emitters (PTBIBI and MCFBIBI), showing good thermal and photophysical properties. The resulting devices have very low turn-on voltage \( (V_{on} = 3.2 \text{ & } 3.1 \text{ V}) \), while deep-blue electroluminescence (EL) with peaking emission wavelength at 434 and 432 nm and CIE coordinates \( (0.15, 0.08 \text{ and } 0.16, 0.06, \text{ which are very close to the pure deep blue NTSC standard}) \).
In addition, the OLED devices with PTBIBI and MCF-BIBI emitters display maximum luminance of 6599 cd m\(^{-2}\) and 3305 cd m\(^{-2}\), the current efficiency of 1.95 and 1.54 cd A\(^{-1}\), maximum power efficiency of 1.59 and 1.39 lm W\(^{-1}\), and maximum external quantum efficiency of 3.59% and 2.67%, respectively.

2. Molecular design

The careful selection of donor and acceptor is very important in developing deep-blue emitters with HLCT excited states character in D-\(\pi\)-A system. To have both LE and CT in excited states can be simultaneously achieved by connecting the mild donor (D) and mild acceptor (A) in the molecular structure with push–pull strength, which controls the CT energy close to LE energy. Benzilimidazole is known for the deep blue emitters with less FWHM. By virtue of the nitrogen atom in the imidazole ring, it acts as a mild donor when it is attached to a mild acceptor such as benzimidazole, which is known for its good electron-transporting properties [33, 34]. The different substituent at the N1 position of imidazole, as the N1 position enhances the orbital coupling interaction, is because of the perpendicular transition directions of the LE and CT states. It also enables more CT components to transform or convert into singlet excitons to improve the EL efficiency and tune molecular excited states properties. Prior to synthesis, the electronic features were understood by means of computational methods (density functional theory (DFT) and time-dependent density functional theory (TD-DFT)).

3. Theoretical calculation

In order to study quantum chemical properties, ground-state geometries and electronic properties at the molecular level of the designed fluorophores were done using density functional theory (DFT) calculations by implementing the theory B3LYP/6-31G (d, p) basis set [35]. The optimized geometries, frontier molecular orbitals, and electrostatic potential surface of both the fluorophores are shown in Figure 2. The optimized geometries of both imidazole and phenyl spacer indicate fluorophores with a more twisted structure, which ultimately results in emission in the deep-blue to blue regions. It also prevents the intermolecular interactions and aggregations in solid states, which usually lead to either color impurities or, worse, quenching of emission in the solid-state [36]. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied

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**Figure 2.** Optimized structure, frontier molecular orbitals and electrostatic potential surfaces of PTBIBI and MCFBIBI fluorophores.
Table 1. Frontier molecular orbital and excited states energy levels of proposed molecules.

| Fluorophore | HOMO (eV) | LUMO (eV) | HOMO-1 (eV) | LUMO +1 (eV) | E_g (eV) | S_1 (eV) (Gas)/DCM | T_1 (eV) (Gas)/DCM | Oscillatory strength (f) |
|-------------|-----------|-----------|-------------|-------------|---------|------------------|------------------|-----------------------|
| PTBIBI      | -5.138    | -1.454    | -5.564      | -0.894      | 3.69    | 3.326/3.319      | 2.616/2.637      | 1.282                 |
| MCFBIBI     | -5.302    | -1.537    | -5.612      | -1.247      | 3.76    | 3.368/3.357      | 2.627/2.649      | 1.293                 |

molecular orbital (LUMO) energy levels, energy band gaps (E_g), and excited states energy levels (singlet and triplet) are summarized in Table 1. The HOMOs of both the designed materials show almost identical charge distributions, which indicate that the HOMO was mainly located on electron-donating benzimidazole along the long-axis phenyl spacer as in Figure 2. The LUMO in the case of PTBIBI and MCFBIBI is mainly localized on the electron-accepting π-linked aromatic spacer and benzimidazole moiety. The calculated HOMO/LUMO values -5.14/-1.45 eV and -5.30/-1.54 eV and the probable HOMO–LUMO energy gap (E_g) 3.69, and 3.76 eV for PTBIBI and MCFBIBI, respectively, and the resulting data are presented in Table 1. However, the transition from HOMO to LUMO in PTBIBI and MCFBIBI is allowed due to the efficient overlap in the frontier molecular orbitals (FMOs) Fig. S22. The complete spatial separation in FMOs is promising for carrier injection charge transporting properties. Consequently, it is advantageous for obtaining high-performance OLED devices [37].

Figure 3. Natural transition orbital pairs with (HONTOs and LUNTOs) transition character analysis for singlet states (S_1-S_10) of PTBIBI (f-osccillator strength and % weights of hole-particle).
Additionally, the ground state electronic cloud distribution was also investigated by using an electrostatic potential (ESP) map for PTBIBI and MCFBIBI as shown in Figure 2. The most negative potential was found to be distributed on an electron-deficient pyridine-like nitrogen atom (\(-N=\)) having two lone-pair electrons for both the fluorophores. While the positive site populated around the phenyl ring has pyrrole-type nitrogen (blue cloud on ESP map), similarly, the phenyl ring fused on 4–5 position of imidazole ring appears to have neutral electrostatic potential over the two terminals of molecules (green/yellow cloud on ESP map). The calculated vertical excitation wavelengths, orbital contribution, and the oscillator strength (\(f\)) of the fluorophores are listed in Table ST4. Atom coordinates of all the synthesized fluorophores are given in the supplementary information (S16).

Moreover, the excited states’ electronic transitions, natural transition orbitals (NTOs) and the related weight for the first 10 singlets and triplet excited state [38] as evaluated with the particle-hole pair contribution of PTBIBI are shown in Figure 3. The results show a hybrid splitting state character from the coupling of LE and CT levels to form HLCT (Table 2). The NTOs pair with the transition character of MCFBIBI are shown in Fig. S24, respectively, while the corresponding are presented in Table ST3. In the case of PTBIBI, excitation, the ‘hole’ was localized on benzilimidazole and N1-substituted phenyl ring, whereas the ‘particle’ was distributed on both imidazole and a small contribution at the phenyl ring attached to both the imidazole. The GS excitation transition reveals the hybrid states because the hole and particle are perpendicular to each other, forming HLCT state with lower oscillatory strength (\(f_{S_0\rightarrow S_3} = 0.0516\)). In the case of MCFBIBI, the transition direction was found along the phenyl spacer toward the C2-substituted direction and revealed as CT and LE, respectively. The GS \(\rightarrow S_3\) excitation transition in the case of MCFBIBI suggests that the CT constituent is perpendicular to LE in the mix transition and generates hybrid HLCT states with lower oscillatory strength (Table 2).

### 4. Synthesis

The designed blue emissive materials PTBIBI and MCFBIBI employ imidazole derivatives as mild electron donor (D) and mild acceptor (A), i.e. D benzilimidazole (BI) having a different substituent at N1-position and a benzimidazole (BI), respectively. The synthetic route is shown in Scheme 1 [39, 40]. BBI-Br, Intermediates-I, Fig. S1 were synthesized by Suzuki coupling reaction and 4′-bromo-[1,10-biphenyl]-4-carbaldehyde, and Intermediates-II Fig. S1 as well as all the targeted fluorophores were synthesized by Suzuki coupling reactions.

#### 4.1. Synthesis of 2′-(4′′-(1-(4-(tert-butyl)phenyl)-4,5-diaryl-1H-imidazol-2-yl)′-1′′-terphenyl)-4-yl)-1-phenyl-1H-benzo[d]imidazole (PTBIBI)

20 mL toluene, 10 mL ethanol and 8 mL Na2CO3 (2M) aq. were added to a mixture of 229.6 mg 2′-(4′-bromo-...
Scheme 1. Synthetic routes and molecular structure of the designed blue emitters PTBIBI, MCFBIBI.

[1,1′-biphenyl]-4-yl)-1-phenyl-1H-benzo[d]imidazole (BBI-Br, 0.54 mmol), 300 mg 1-(4-((tert-butyl)phenyl)-4,5-diphenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-imidazole (PTBIPin) (0.54 mmol) and 31.0 mg Pd(PPh3)4 (0.0276 mmol). The suspension was heated to 90 °C with stirring under an argon atmosphere. After 24 h, the mixture was allowed to cool to room temperature, extracted with CH2Cl2 and dried over anhydrous MgSO4 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 a white solid (71.5%).

1H-NMR (400 MHz, CDCl3, TMS, δ ppm) 7.90 (d, J = 7.2 Hz, 1H), 7.73–7.44 (m, 16H), 7.36 (d, J = 6.5 Hz, 3H), 7.25 (dt, J = 17.3, 8.5 Hz, 10H), 7.14 (s, 2H), 7.00 (d, J = 6.7 Hz, 2H), 1.28 (s, 9H). 13C-NMR (100 MHz, CDCl3, TMS, δ ppm) 152.05, 151.63, 146.56, 143.10, 141.41, 139.73, 139.13, 138.44, 137.40, 137.12, 134.59, 134.46, 131.41, 131.14, 130.72, 129.97, 129.87, 129.23, 128.90, 128.67, 128.26, 128.17, 127.93, 127.87, 127.53, 127.48, 127.40, 127.38, 126.76, 126.54, 126.02, 123.40, 123.06, 119.86, 110.46, 34.70, 31.28. MALDI-TOF (m/z): [M+H]: 773.38 calculated for C56H44N4: 773.36.

4.2. Synthesis of 2-(4″-(4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazol-2-yl)-[1,1′:4′,1″-terphenyl]-4-yl)-1-phenyl-1H-benzo[d]imidazole (MCFBIBI)

The synthetic procedure of MCFBIBI was same as that of compound PTBIBI. White MCFBIBI powder yield was (75.2%). 1H-NMR (400 MHz, CDCl3, TMS, δ ppm) 7.90 (d, J = 8.0 Hz, 1H), 7.69–7.61 (m, 7H), 7.60–7.45 (m, 10H), 7.44–7.19 (m, 15H), 7.13 (d, J = 7.0 Hz, 2H). 13C-NMR (100 MHz, CDCl3, TMS, δ ppm) 152.02, 146.55, 143.04, 141.34, 140.47, 139.55, 139.29, 138.78, 137.37, 137.35, 137.07, 134.05, 131.14, 130.12, 129.97, 129.86, 129.78, 129.35, 129.07, 128.90, 128.67, 128.62, 128.40, 128.24, 127.50, 127.43, 127.40, 127.36, 126.86, 126.81, 126.77, 125.35, 123.40, 123.06, 119.82, 110.45. 19F-NMR (376 MHz, CDCl3, TMS, δ ppm) -62.95 MALDI-TOF (m/z): [M+]: 785.13 calculated for C56H44N4: 785.28.

5. Results and discussions

5.1. Thermogravimetric analysis

Thermal stabilities of synthesized fluorophores were studied by using thermalgravimetric analysis (TGA) in
the presence of an inert atmosphere (at a scan rate of 10°C min⁻¹). TGA curves of fluorophores are shown in Figure 4, while the corresponding data are listed in Table 4. Figure 4 indicates that the synthesized fluorophores possess great thermal stabilities. The thermal degradation temperature (5% weight loss) for PTBIBI and MCFBIBI was found to be 226 and 410°C due to the rigid and bulky structure of benzilmidazole and BI, which is the primary characterization needed for OLED applications. The results suggest that presently studied fluorophores highlight high decomposition temperature. It is the prerequisite for OLEDs since high Td enhances the lifetime of the devices.

5.1.1. Electrochemical properties

The energy levels and electrochemical analysis of all the fluorophores were studied by using cyclic voltammetry (CV) measurements. The cyclic voltammograms are shown in Figure 5, and the related data are shown in Table 3. Figure 5 revealed that the fluorophore has distinct redox behavior, which strongly indicates that the fluorophores have capability charge carrier transporting properties. In agreement with onset potentials, the HOMO and LUMO energy levels were calculated using Equations (1) and (2) [41].

\[ E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.4)\text{eV} \quad \text{(1)} \]
\[ E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{red}} + 4.4)\text{eV} \quad \text{(2)} \]

Table 3. Electrochemical properties of all the fluorophores.

| Fluorophore | \( E_{\text{onset}}^{\text{ox}} \) (V) | \( E_{\text{onset}}^{\text{red}} \) (V) | HOMO (eV) | LUMO (eV) | \( E_g^a \) (eV) | \( E_g^d \) (eV) |
|-------------|-----------------|------------------|-----------|-----------|---------------|---------------|
| PTBIBI      | 1.23            | -1.41            | -5.63     | -2.99     | 2.64          | 3.73          |
| MCFBIBI     | 1.32            | -1.64            | -5.72     | -2.76     | 2.96          | 3.83          |

Notes: a, Onset oxidation potential. b, Onset reduction potential. c, Electrochemical bandgap determined from cyclic voltammetry. d, Optical bandgap estimated from neat thin-film DRS.

and \(-5.72/-2.76\) eV, with an energy difference between HOMO and LUMO (bandgap \( E_g \)) of 2.64 and 2.94 eV, respectively. From the data, it is clear that all the fluorophores showed a wide bandgap in the solution, which is a good indicator for the development of deep blue OLEDs.

5.1.2. Optical properties

The optical properties of the synthesized deep blue fluorophores were measured using the UV-VIS spectrophotometer and the photoluminescence PL spectra using a spectrofluorometer. The absorption spectra were recorded in THF (10⁻⁵ M) and spin-coated neat thin-film, whereas the PL spectra in THF (10⁻⁵ M), spin-coated neat film, and solid states as shown in Figure 6 and the key photophysical data are presented in Table 4. The UV-VIS spectra of synthesized deep blue materials show nearly similar absorption behavior in the range of 229–310 nm in the solution phase (Figure 6(a)). It is observed that the absorption bands in the range of 229–275 nm in the higher energy end could be attributed to the \( \pi - \pi^* \) transitions of benzilimidazole and phenyl rings [43, 44]. However, strong absorption bands at around 333-341 nm could be assigned to the \( \pi - \pi^* \) transitions as well as in intramolecular charge transfer (ICT) between benzilimidazole and benzimidazole (BI) moiety. This is in spite of the strong absorption bands in the case
of a neat thin film of three fluorophores that were found to be broad and observed to occur at around 300-304 nm with a peak at around 351 nm. Also, the absorption bands in the thin film were found to red-shift compared to that in solution due to aggregation and their relative π-π stacking interactions in the solid, as shown in Figure 6(b) [45]. Diffuse reflectance spectra (DRS) (using neat thin film) of both the synthesized deep blue fluorophores were carried out to evaluate the optical bandgap of the fluorophores by employing the Kubelka–Munk function [46] (Figure 7(b)) and the resulting values are tabulated in Table 3. The bandgaps obtained from the DRS spectra are in good alignment with the theoretically calculated bandgaps.

The PL spectra of the new blue emissive materials in solution are shown in Figure 6(a), and those in neat thin film and solid are shown in Figure 6(b). The corresponding data are summarized in Table 4. All the synthesized fluorophores show deep blue emission in the dilute solution with peaking wavelengths at 434 and 425 nm for PTBIBI and MCFBIBI, respectively, as displayed in Figure 5(a). The CIE color gamut of PTBIBI and m-CFBIBI are shown in Fig. S21. The corresponding CIE color coordinates (x and y) of all the fluorophores are tabulated in Table ST1. However, the PTBIBI and MCFBIBI show negligible red shift emission in the thin film as well as in solid state compared to that in solution. This observation clearly indicates that the intermolecular interaction in solid states was controlled effectively because of the rigid molecular structure and highly twisted geometries of PTBIBI and MCFBIBI [47]. From Figure 6 and Table 4, one can deduce that the PL emission of the MCFBIBI shows slight blue shift emission compared to that of PTBIBI in solution, thin-film, and solid states because of the bandgap of MCFBIBI is higher than that of PTBIBI.

The absolute quantum yields (Φ) of fluorophores were also measured in the solution as well as in a neat thin film by using the integrating sphere. The quantum yield results of all the synthesized fluorophores in the solution and neat thin film are tabulated in Table 4. All the molecules showed excellent quantum yield, which is essential for efficient blue OLEDs. The PTBIBI and MCFBIBI showed higher quantum yields in the solution and solid 97.1%/77.3% and 91.9%/58.9%, respectively. The higher quantum yield supports the existence of co-emission of LE and CT of synthesized fluorophores.

To further study the excited state properties of fluorophores, time-resolved PL decay of molecules with the concentration of 10^{-5} M in chloroform solution were examined using the time-correlated single-photon counting (TCSPC) technique under excitation by a suitable laser source and decays of the blue emissive materials as shown in Figure 7(a). The decay curves were fitted with mono-exponential function, and the lifetime of all the synthesized fluorophore were calculated by using

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**Figure 6.** Normalized UV-VIS absorption spectra and PL spectra (a) in THF solution (10^{-5} M), (b) Normalized UV-VIS absorption spectra of neat film and PL spectra of neat film and solid of PTBIBI and MCFBIBI.

**Table 4.** Key photophysical properties of all synthesized fluorophores.

| Fluorophore | Solution | Thin film | Solid |
|-------------|----------|-----------|-------|
|             | $T_d$ (°C) | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\Phi_{FS}$ (%) | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\Phi_{FT}$ (%) | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) |
| PTBIBI      | 410      | 231, 275, 333 | 434 | 97.1 | 304, 352 | 437 | 77.3 | 393 | 438 |
| MCFBIBI     | 226      | 229, 261, 341 | 425 | 91.9 | 300, 351 | 428 | 58.9 | 376 | 433 |

$T_d$ = Thermal decomposition temperature corresponding to 5% weight loss, $\lambda_{abs}$ = absorption maximum, $\lambda_{em}$ = emission maximum, $\lambda_{ex}$ = excitation maximum, $\Phi_{FS}$ = Absolute fluorescence quantum yield in CHCl_3 (10^{-5} M), $\Phi_{FT}$ = Absolute fluorescence quantum yield in thin film.
Equation (3)

\[ \tau = I_0 + A_1 \exp \left( -\frac{t}{\tau} \right) \]  
\( (3) \)

where \( I_0 \) is the offset value (\( I_0 = 0 \)), \( A_1 \) is the scalar quantity obtained from the curve fitting, \( t \) is the time in ns and \( \tau \) is the exponential decay time. The resulting fluorescence lifetime values of all the synthesized fluorophores were tabulated in Table S1.2. The one lifetime decay profile indicates that it may have LE and CT states in the \( S_1 \) state, which are highly mixed or hybridized, further indicating HLCT in the \( S_1 \) state of all the molecules [48].

5.2. Solvatochromism

The effect of solvents on the synthesized fluorophores was thoroughly studied with the help of solvatochromism experiments. Here, solvents ranging from non-polar to polar were selected to further investigate the intramolecular charge transfer (ICT). The absorbance and PL emission of newborn fluorophores were performed using different solvents: hexane, toluene, tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), and dimethylsulfoxide (DMSO) as shown in Figure 8.

From Figure 8, it is clear that increasing the solvent polarity does not exert any significant influence on the absorbance spectra of all the fluorophores. In contrast, PL emissions indicate a bathochromic shift from low polarity to high polarity solvents, indicating that ICT in the fluorophores. The PL emissions show a redshift of 78 and 66 nm from non-polar to polar for PTBIBI and MCFBIBI, respectively. Along with increasing polarity, FWHM also increased with a broadening of the PL emission peaks and clearly indicating CT in excited states of all fluorophores [49]. Detailed photophysical data are tabulated in Table 5.

Additionally, it is observed that the PL emissions spectra in hexane and toluene show two fine vibrational structure spectra that reveal the locally excited (LE) feature of excited states in a non-polar solvent. With increasing polarity after toluene, the emissions peak becomes non-vibrational and keeps this until DMSO is used, which also indicates CT in excited states [50]. This outcome may indicate that the LE and CT state are lying close, so a slight change in the solvent polarity CT character dominates in excited states [51]. Furthermore, the influence of the solvent environment on the photophysical properties of fluorophores can also be understood by using the Lippert-Mataga equation, 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 (4) and (5) of Lippert-Mataga set out the Stokes’ shift (cm\(^{-1}\)) as a function of the change in dipole moment (\( \Delta \mu_{ge} = \mu_e - \mu_g \)) [52, 53].

\[
\hbar c (\nu_a - \nu_f) = \hbar c (\nu_a^0 - \nu_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3} \alpha (\varepsilon, n) \]  
\( (4) \)

where \( (\nu_a^0 - \nu_f^0) \) refers to the Stokes’ shifts (in cm\(^{-1}\)) between the absorption and fluorescence emission maxima \( [\nu_a^0 = 1/\lambda_{abs}(\text{max}), \nu_f^0 = 1/\lambda_{em}(\text{max})] \), \( \hbar \) is Planck’s constant, \( c \) is the velocity of light, \( \mu_e \) and \( \mu_g \) are the dipole moment in excited states and ground states.

\[
\Delta f = f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \]  
\( (5) \)

\[
a = \left( \frac{3M}{4N\pi\alpha} \right)^{\frac{1}{2}} \]

where \( \Delta f \) is the orientation polarizability of solvents, \( \alpha \) is the solvent cavity radius derived from the Avogadro’s
number \( N \), molecular weight \( M \), and the density \( d = 1.0 \text{ g/cm}^3 \). \( \varepsilon \) and \( n \) refer to the solvent dielectric and solvent refractive indices, respectively. The plot was drawn from Stokes’ shift as a function of orientation polarizability \( \Delta f \) [54, 55]. Figure 9 shows the linear relationship of Stokes’ shift and orientation polarizability of PTBIBI and MCFBIBI in different solvents. The corresponding data are summarized in Table 5. From the Figure 9 correlation coefficient \( R^2 \), slope, and intercept noted for PTBIBI and MCFBIBI are \( R^2 = 0.8489 \) and 0.9257, slope = 11,184 cm\(^{-1}\) and 11,523 cm\(^{-1}\), and intercept = 4840 and 4211 cm\(^{-1}\), respectively.

### Table 5. Key photophysical properties of PTBIBI and MCFBIBI.

| Solvents | \( \Delta f \) | \( \lambda_{abs} \) (nm) | \( \lambda_{em} \) (nm) | Stoke’s shift (cm\(^{-1}\)) | FWHM (nm) | \( \lambda_{abs} \) (nm) | \( \lambda_{em} \) (nm) | Stoke’s shift (cm\(^{-1}\)) | FWHM (nm) |
|-----------|----------------|-----------------|------------------|------------------------|-----------|-----------------|-----------------|------------------------|-----------|
| Hexane    | 0.0012         | 338             | 397              | 4400                   | 58        | 340             | 397              | 4220                   | 58        |
| Toluene   | 0.0131         | 330             | 406              | 5670                   | 62        | 342             | 402              | 4360                   | 59        |
| THF       | 0.210          | 339             | 434              | 6440                   | 75        | 338             | 425              | 6060                   | 72        |
| ACN       | 0.305          | 332             | 465              | 8620                   | 101       | 330             | 449              | 7590                   | 94        |
| DMF       | 0.276          | 341             | 462              | 7680                   | 102       | 339             | 452              | 7390                   | 96        |
| DMSO      | 0.263          | 342             | 475              | 8180                   | 105       | 339             | 463              | 7890                   | 99        |

### 5.2.1. Electroluminescence properties

The theoretical, photophysical and electrochemical properties of the deep blue emissive materials encouraged us to further explore possible applications in high-performance deep-blue OLEDs. Since the PTBIBI and MCFBIBI emitters showed high thermal stability and good photophysical properties, we have evaluated electroluminescence (EL) properties by fabricating and characterizing doped blue OLED devices. Multilayer OLED devices with a device configuration of 1 nm of molybdenum oxide MoO\(_3\), 35 nm of 4,4′-bis(9H-carbazol-9-yl)biphenyl (CBP), 3 nm of MoO\(_3\) and an emission layer...
Figure 10. Device configuration and the chemical structures of materials used in the OLED device.

(15 nm) consisting of CBP with PTBIBI & MCFBIBI (10 wt%), 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 are sequentially deposited on Glass/ITO substrates. The device configuration and structure of materials used in the device fabrication process are shown in Figure 10.

The devices based on PTBIBI and MCFBIBI emit EL emission centered at 434 and 432 nm with the Commission Internationale de l’Eclairage (CIE) coordinates of (0.15, 0.06) and (0.16, 0.06), respectively. The emission spectrum resembles the PL emission spectra of the vacuum-deposited films, indicating good exciton confinement in the emission layers and electroluminescence due to PTBIBI and MCFBIBI molecules, as shown in Figure 11.

Figure 12 shows current–voltage-luminance (J-V-L) characteristics of the OLED devices fabricated with these two emitters. The blue emitting OLED devices have a low turn-on voltage of 3.2 and 3.1 V (corresponding to blue bandgap). Relevant display luminance of 100 cd/m² can be achieved at a voltage of 5.8 and 6 V and maximum luminance of 6599 cd/m² & 3305 cd/m² is recorded at 15 V, respectively. The PTBIBI molecule has superior performance over the MCFBIBI molecule, consistent with superior optoelectronic properties exhibited by thin films. HOMO and LUMO levels of PTBIBI &

Figure 11. Comparison of thin-film PL and EL spectra for PTBIBI and MCFBIBI emitters.

Figure 12. J-V-L characteristics for OLED devices with PTBIBI and MCFBIBI emitters.

Figure 13. Current efficiency-lumiance-EQE plot for OLED devices with PTBIBI and MCFBIBI emitters.
Table 6. EL performance of blue OLEDs based on PTBIBI and MCFBIBI emitters.

| Dopant  | max (nm) | Turn on voltage (V) @1 cd m⁻² | PE₁₀₀/CE₁₀₀/EQE₁₀₀ (lmW⁻¹/cdA⁻¹/%) | PE₁₀₀₀/CE₁₀₀₀/EQE₁₀₀₀ (lmW⁻¹/cdA⁻¹/%) | PE_max/CE_max/EQE_max (lmW⁻¹/cdA⁻¹/%) | CIE coordinates | L_max (cdm⁻²) @15V |
|---------|----------|-------------------------------|----------------------------------|--------------------------------------|--------------------------------------|----------------|------------------|
| PTBIBI  | 434      | 3.2                           | 1.01/1.18/3.42                   | 0.65/1.77/3.35                      | 1.59/1.95/3.59                      | (0.15, 0.06) | 6599             |
| MCFBIBI | 432      | 3.1                           | 0.62/1.18/2.25                   | 0.36/1.09/2.15                      | 1.39/1.55/2.67                      | (0.16, 0.06) | 3305             |

MCFBIBI, which were measured via CV, were -5.63 and -5.72 eV and -2.99 and -2.76 eV for PTBIBI and MCFBIBI molecules, respectively. CBP host has HOMO and LUMO of 6.0 and 2.9 eV and triplet energy of 2.5 eV. The current efficiency and external quantum efficiency (EQE) of OLED devices are shown in Figure 13. Table 6 lists all the key parameters of the OLED devices, comparing the OLED devices with the two emitters. The OLED devices for PTBIBI & MCFBIBI display current efficiency of 1.95 and 1.54 cd A⁻¹, maximum luminous power efficiency of 1.59 & 1.39 lm W⁻¹, and maximum external quantum efficiency of 3.59 & 2.67%, respectively. In addition, the efficiency roll-off for the fluorophores is discussed with respect to reported blue fluorophores (details are given in the supplementary information).

6. Conclusions

In summary, two thermally stable D-π-A fluorophores were designed and synthesized by connecting two different imidazole having π spacer between the benzimidazole (D) and benzimidazole (A) moiety with HLCT character. Both the synthesized fluorophores show deep blue emission with good PLQY in the solution as well as in solid states. The theoretical (NTOs) and experimental (solvatochromism) studies show these materials possess the LE and CT hybrid states. Moreover, these fluorophores were used as dopant materials, and doped devices were fabricated. Both the emitters showed deep blue emission with CIEy value of 0.06 with a very low turn-on voltage of < 3.27 V. Among the two, the doped device based on the PTBIBI shows good EL performance because it shows maximum external quantum efficiency of 3.59% with CIE coordinates of (0.15, 0.06) at 1000 cd m⁻² and maximum luminance of 6559 cd m⁻².

Disclosure statement

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

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Supplementary material

Supporting information includes NMR spectra (¹H, ¹³C, and ¹⁹F), and mass spectra of the compounds, as well as the CIE coordinates for the compounds in solutions, thin-film and solid phase, TD-DFT and vertical transition and atom coordinate of all the fluorophores.

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