Solution-processed deep-blue (y ~ 0.06) fluorophores based on triphenylamine-imidazole (donor-acceptor) for OLEDs: computational and experimental exploration

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ABSTRACT
Developing solution-processable deep-blue emitters for organic light-emitting diodes (OLEDs) is still a challenging task. In this context, two new solution-processable deep-blue emitters, N,N-diphenyl-4’-(1-(3-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1’-biphenyl]-4-amine (4-PIMCFTPA) and 4’-(4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazol-2-yl)-N,N-diphenyl-[1,1’-biphenyl]-4-amine (4-BICFTPA), were successfully designed and synthesized by incorporating phenanthroimidazole (PI)/diphenylimidazole (BI)-triphenylamine (TPA), which is functional at the N1 position of the imidazole, with Ph-mCF3. The thermal, photophysical, and electrochemical properties of both fluorophores were systematically explored. These fluorophores showed a deep-blue emission in the solution as well as in the solid state. The highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) energy level of the fluorophores was calculated using electrochemical studies and compared with the theoretical calculation [the density functional theory (DFT)]. The asymmetrically twisted conformation of 4-PIMCFTPA between PI-TPA efficiently showed a high photoluminescence quantum yield. OLED (undoped and doped) devices were fabricated with the newly synthesized emitters, and 4-PIMCFTPA demonstrated better electroluminescence (EL) performance than the BI-based emitter. Thus, the OLED based on 4-PIMCFTPA (1 wt% in the CBP host) had the best EL performance, with a maximum external quantum efficiency 1.7% and CIE coordinates of (0.17, 0.06).

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1. Introduction
Organic optoelectronic devices with π-conjugated effi- cient materials have been the most attractive opto- electronic devices because of their superficial and cost-efficient synthetic methodologies. They have often showed simply adaptable electrical and photophysical behavior [1–6]. Perception of the structure–function correlation in such organic materials and understanding of the techniques for controllably tuning their multipurpose characteristics play vital roles in their use for various applications, including for organic polymer-based solar cells (OPVs), organic fluorophores-based light-emitting diodes (OLEDs), electronic semiconductors (field-effect transistors), and molecular sensors [7–9]. Currently, OLEDs are attracting much attention because of their empirical use in smart-generation flat-panel displays and lighting applications (large-screen televisions and smartphones). Ongoing studies promote the use of smart OLEDs as versatile solid-state lighting (SSL) sources for smart displays. In high-performance displays, it is highly essential to have an appropriate balance of the three primary colors [red, green, and blue (RGB) mixing]. To date, several optoelectronic materials with efficient red and green emissions for high-performance OLEDs are being given emphasis. However, the development of efficient deep emitters for stable blue OLEDs with Commission Internationale de L’Eclairage (CIE) coordinates that match the National Television System Committee (NTSC) blue standard of (0.14, 0.08) is still a chal- lenging task [3]. Moreover, efficient deep-blue emitters are imperative because they can directly or indirectly cut down the power consumption of full-color display
devices and further promote emissions in the higher-wavelength region [10–15]. However, their wide band gap (almost > 3 eV) is often tough for the charge-injection phenomenon, disrupts the proper balancing of the charge-carrier (hole/electron) flow, and eventually destabilizes the device performance of OLEDs.

The emitting layer allows for successful investigation of first-generation fluorescent emitting materials whose 25% internal quantum efficiency (IQE) [16] can be significantly upgraded to 100% by second-generation phosphorescent materials [17–21] and third-generation TADF materials [22–24]. However, both phosphorescent and TADF materials have shown effective (100%) harvesting of the dark triplet excitons to the ground state, which improves the device performance. However, some serious difficulties remain for the latter two cases. The short lifetime of TADF OLEDs and the phosphorescent operation lifetime are still major limitations of blue OLEDs. They degrade the phosphorescent materials because of their wide band gap (≈ 3 eV) and long exciton lifetime (≈ μs), as well as the hot excited state (≈ 6 eV) created by the exciton-polaron interactions [25]. The high triplet energy and long triplet lifetime is generally caused by the short lifetime of blue OLEDs in TADF organic materials. Hence, the development of both highly efficient phosphorescent and TADF-based OLEDs, which scarcely fall into the deep-blue region, remains a forbidding challenge that corresponds to green and red components. Due to the unbalanced hole-electron movement and intrinsic wide band gap in blue OLEDs, they are superior and versatile than green and red emitters. Blue OLEDs generally correspond to the CIE coordinates of y < 0.15 and (x + y) < 0.30 [3]. Moreover, fluorescent OLEDs are fascinating and continue to gain much attention because of their long operational lifetimes and the high color excellence of their electroluminescence (EL), which make them ideal for manufacturing cost-effective full-color displays for next-generation smart display and lighting applications.

According to material chemists, triphenylamine (TPA) is a productive structural entity whose performance is promising for molecular materials due to its rigidity, high thermal stability, photoexcitation and morphological stabilities, and better hole-transporting capacity [26–29]. Furthermore, the frontier molecular orbital of TPA moieties has the highest occupied molecular orbital (HOMO), which enables efficient hole injection compared to other moieties and a work function near that of indium tin oxide (ITO) or N,N′-Di(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB), which are generally used as hole-transporting materials [30]. Currently, however, phenanthroimidazole/diphenylimidazole-based moieties are widely used to make deep-blue fluorophores due to their wide absorption and bright luminescent property [31–33]. Combinations of imidazole-based derivatives with TPA assist as effective donor-π-acceptor (D-π-A) bipolar materials [34]. Hence, the planning and synthesis of imidazole’s moieties with upgraded functional fluorophores are very important to refine their optical and charge transport properties in devices.

In 2012, Tong et al. used phenanthroimidazole (electron-transporting moiety) as the acceptor core and TPA (hole-transporting moiety) as the good donor through different linking arrangements in the core structure (BPA-BPI, PATPA) shown in Figure S1. These reported fluorophores showed deep-blue emissions with good QYs. The OLED device based on these fluorophores showed the following efficiencies: a maximum current efficiencies (CEmax) of 0.65 and 0.34 cd/A; maximum power efficiencies (PEmax) of 0.68 and 0.24 lm/W; and maximum external quantum efficiencies (EQEmax) of 0.55% and 0.72%, with deep-blue CIE coordinates of (0.15, 0.05) and (0.15, 0.06), respectively [35]. Recently, diphenylimidazole (as the acceptor) and TPA (as the donor) have been synthesized to design bipolar materials by directly linking the donor and the acceptor without a spacer (BIMTPA and BIPTPA). The structure is shown in Figure S1. These fluorophores also showed deep-blue emissions in a solution, and the OLED device performance of 1% doped in the host showed efficiencies of CEmax = 0.30 and 0.50 cd/A, PEmax = 0.10 and 0.20 lm/W, and EQEmax = 0.2% and 0.4%, with sky-blue CIE coordinates of (0.21, 0.25) and (0.17, 0.15), respectively [36,37].

In this study, we incorporate TPA as the hole-transporting (electron-rich) moiety and phenanthroimidazole/diphenylimidazole as the electron-transporting moiety using one phenyl ring between the donor and the acceptor (as the spacer) to realize efficient bipolar materials. Moreover, we substitute the N1 position of the imidazole with that of the electron-withdrawing group (m-Ph-CF3) to fine-tune the emission near the blue region, and with that of the electron-withdrawing (-CF3) group to enhance the electron-accepting capability of the imidazole moiety. Hence, we will boost both the efficiency and the electron-transporting properties of the device. Before synthesizing the targeted fluorophores, to understand their electronic and optical properties, we performed a computational investigation. The calculation revealed that all the fluorophores were twisted in nature and showed a wide energy band gap (Eg > 3.1 eV; for blue: ~3.0 eV) and triplet energy (T1 > 2.46 eV). Moreover, the spatial distributions of the frontier molecular orbitals showed the bipolar properties of the targeted fluorophores, which encouraged us to synthesize
them. We structurally confirmed the synthesized materials with spectroscopic techniques. The photophysical properties of the fluorophores changed according to the acceptor core. Both the fluorophores showed blue emissions with good QYs in the solution and solid phases. We performed cyclic voltammetry analysis to determine the low- and high-lying HOMO–LUMO energy levels for the optimization of the devices. We also examined the fluorophores as blue-emitting dopants in solution-processed multilayer OLEDs, which showed good device performance and blue EL emissions that approached the NTSC standard.

2. Theoretical calculations

To gain a better insight into the structural properties of the fluorophores at the molecular level, we studied their ground state geometries and electronic properties using the density functional theory (DFT), and we performed the time-dependent DFT (TD-DFT) calculation using a B3LYP/6-31G (d, p) basic set [38]. Figure 1 shows the optimized structure of all the synthesized fluorophores in the gas phase. It clearly reveals that all the fluorophores had a twisted conformation, which suppressed the π-conjugation and so kept the emission at the higher energy end and thus, supported the achievement of the emission in the deep-blue to blue region. Moreover, the twisted structure reduced the aggregation and the intermolecular charge transfer in the solid state, which usually affects the color purity and quenches the emission in the solid state [39]. The frontier molecule orbitals, lowest unoccupied molecular orbitals (LUMO), and HOMO are shown in Figure 2. The calculated HOMO–LUMO energy levels, energy band gaps (Eg), and first excited state energy levels of the fluorophores are listed in Table 1. The complete separation of the HOMO–LUMO energy levels in 4-PIMCFTPA and 4-BICFTPA is favorable for achieving effective hole- and electron-transporting properties because it can create a charge-hopping channel between the hole and the electron, which may endow the fluorophores with bipolar charge transport ability in the device that will improve the EL performance of the OLEDs [40,41,42]. Table 1 shows the energy differences in the HOMO and LUMO of both fluorophores; and in Figure 2, the electron cloud distribution points out that the HOMO levels of both fluorophores were mainly localized in the electron-rich triphenylamine (TPA) moiety and phenyl spacer as well as in the imidazole ring. The LUMOs of the 4-PIMCFTPA were completely localized on the imidazole-N1 substituted (m-Ph-CF3) moiety, whereas the LUMOs of 4-BICFTPA were distributed in diphenylimidazole to the N1-substituted (m-Ph-CF3) moiety with a small π-bridge. The estimated HOMO/LUMO energy levels of the synthesized fluorophores are -4.97/-1.57 eV (4-PIMCFTPA) and -4.95/-1.47 eV (4-BICFTPA), respectively. The estimated HOMO–LUMO energy gaps (Eg) for 4-PIMCFTPA and 4-BICFTPA were 3.40 and 3.48 eV, respectively (Table 1).

The energy gap of 4-BICFTPA was slightly higher than that of 4-PIMCFTPA, due to the well-separated HOMO–LUMO that was distributed over the donor (TPA) and the acceptor (BI), respectively, which generated the allowed electronic transitions. The absorption spectra of the newborn emitters were theoretically studied using the TD-DFT method. The computed vertical transition, orbital configuration, and oscillatory strength (f) of the fluorophores are shown in Table S2. The orbital distribution for each state was also calculated. These results impart complete information on the absorption spectra. The simulated absorption spectra of both fluorophores are shown in Figures S20 and S21 [in the gas and dichloromethane (DCM) phases]. The atom coordinates of the fluorophores are given in SI7.

Figure 1. Optimized structures of the fluorophores.
3. Experimental methodology

3.1. Synthesis of N,N-diphenyl-4′-(1-(3-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1'-biphenyl]-4-amine (4-PIMCFTPA)

A mixture of 4-PI-MCF3-Br (0.500 g, 0.97 mmol), (4-diphenylamino)phenyl)boronic acid (0.308 g, 1.06 mmol), Na2CO3 (2.0 M aqueous solution, 10 ml), toluene (20 ml), and ethanol (10 ml), with Pd(PPh3)4 (0.055 g, 0.048 mmol) acting as the catalyst, was refluxed at 90°C in nitrogen atmosphere for 24 h. The resulting solution was cooled to room temperature, after which 30 ml water was added to it, and the mixture was extracted with DCM. The organic phase was dried with anhydrous Na2SO4 and concentrated through rotary evaporation. The residue was purified via column chromatography using an ethyl acetate/petroleum ether mixture as the eluent to obtain the pure product as a white solid. The yield was 76%.

1H-NMR (400 MHz, CDCl3, TMS, δ ppm): 8.90 (d, J = 8.0 Hz, 1H), 8.82 (d, J = 8.4 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.4 Hz, 1H), 7.89 (s, 1H), 7.76–7.48 (m, 7H), 7.34-7.27 (m, 6 H), 7.16–7.11 (m, 6 H), and 7.07 (t, J = 7.6 Hz, 2H). 13C-NMR (100 MHz, CDCl3, TMS, δ ppm): 150.84, 147.68, 147.53, 141.13, 139.48, 137.76, 133.65, 132.69, 130.90, 129.79, 129.34, 128.34, 128.26, 127.90, 127.68, 127.45, 127.05, 126.58, 126.48, 126.41, 125.89, 125.14, 124.56, 124.37, 123.68, 123.13, 122.85, 122.68, and 120.46. MALDI-TOF (m/z): [M + ] calcd for C46H30F3N3, 681.24, found, 681.43.

Table 1. Calculated frontier molecular energy and excited state energy levels.

| Fluorophores | HOMO (eV) | LUMO (eV) | HOMO-1 (eV) | LUMO+1 (eV) | E2a(eV) | S1 (gas) b(eV) | T1 (gas) b(eV) | Oscillating strength (f) |
|--------------|-----------|-----------|-------------|-------------|--------|---------------|----------------|-------------------------|
| 4-PIMCFTPA   | -4.9718   | -1.5695   | -5.4518     | -1.4288     | 3.40   | 3.1170        | 2.4688         | 0.0014                  |
| 4-BICFTPA    | -4.9588   | -1.4708   | -5.4796     | -1.2588     | 3.48   | 3.1885        | 2.8971         | 0.3414                  |

aTheoretical energy band gap (Eg = HOMO-LUMO). bCalculated at B3LYP/6-31G(d, p) basis set in the gas phase.

Figure 2. Electron density contours of the Frontier Molecular orbitals (FMOs) of the fluorophores.
3.2. **Synthesis of 4’-(4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazol-2-yl)-N,N-diphenyl-[1,1'-biphenyl]-4-amine (4-BICFTPA)**

The synthetic procedure of 4-BICFTPA was the same as that of the compound 4-PIMCFTPA, which was achieved by replacing 4-Pi-MCF3-Br with 4-Bi-MCF3-Br. The yield was 74%. $^1$H-NMR (400 MHz, CDCl$_3$, TMS, $\delta$ ppm): 7.65–7.63 (m, 2H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.47 (tt, $J = 19.5$, 8.2 Hz, 7H), 7.33–7.22 (m, 13H), 7.14 (dd, $J = 8.1$, 3.4 Hz, 7H), 7.06 (t, $J = 7.3$ Hz, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$, TMS, $\delta$ ppm): 147.56, 140.64, 138.69, 137.73, 134.06, 131.73, 131.13, 130.68, 130.15, 129.75, 129.34, 129.31, 128.63, 128.38, 128.25, 127.63, 127.40, 126.35, 124.51, 123.74, 123.06. MALDI-TOF (m/z): [M + ] calcd for C$_{46}$H$_{32}$F$_3$N$_3$, 683.25, found, 684.28.

4. Results and discussion

4.1. **Thermal properties**

High thermal stability of fluorescent emitters is generally essential for the fabrication and the operating stability of organic light-emitting devices (OLEDs). The effect of temperature on the synthesized fluorophores was studied using thermo-gravimetric analysis (TGA) in N$_2$ atmosphere. The TGA analysis was conducted from ambient temperature to 800°C at a scanning rate of 10°C/min. The thermographs of the synthesized new emitters are shown in Figure 3. They show that both fluorophores exhibited good thermal stability and thermal decomposition temperature (Td) at a 5% weight loss (4-PIMCFTPA: 350°C and 4-BICFTPA: 304°C) (Table 2). Higher thermal stability was seen in 4-PIMCFTPA than in 4-BICFTPA due to the presence of a highly rigid aromatic skeleton of phenanthroimidazole, unlike
Figure 3. Thermogravimetric analysis (TGA) curves of the imidazole derivatives.

in diphenylimidazole. In Figure S22, the differential scanning calorimetry (DSC) curves show the morphological stability of the fluorophores, and Figure S22 shows a change in phase with respect to temperature. The glass transition temperatures were 234°C and 133°C for 4-PIMCFTPA and 4-BICFTPA, respectively. These DSC and TGA analysis results suggest that the fluorophores have high decomposition temperatures, which show that they good resistancetothermolysisduetothepresenceoffusedaromaticsrings. Such good resistance to thermolysis enhances the device lifetime and operating stability of the fluorophores.

4.2. Photophysical properties

The study of the ultraviolet (UV) absorption and photoluminescence (PL) of the synthesized fluorophores was carried out in a DCM (10⁻⁵ M) solution and in the solid phase. The obtained key photophysical parameters of the synthesized fluorophores are listed in Table 2. The UV-Vis spectra of the synthesized fluorophores in the solution [Figure 4, (left)] showed different absorption patterns because of the different acceptor cores present in the molecules. The fluorophores showed two absorption peaks. At the higher energy level, the strong (∼300 nm) absorption bands were observed due to the π-π* transitions that originated from the aromatic and imidazole rings. The lower energy absorption peaks for 4-PIMCFTPA (356 nm) and 4-BICFTPA (341 nm) are attributed to the intramolecular charge transfer from triphenylamine (the donor) to imidazole (the acceptor) [43]. Figure 4 (left) shows that the absorption wavelength of 4-BICFTPA blueshifted, unlike that of 4-PIMCFTPA, due to the suppressed π-conjugation. In the solid states in Figure 4 (right), the blue fluorophores show absorption wavelengths at 370 nm (PIMCFTPA) and 359 nm (4-BICFTPA), and the absorption redshifts relative to the solution phase, which reveals that intermolecular π-π* stacking occurred in the solid states [44].

In Figure 5 (left), the PL spectra of the fluorophores show a blue emission that peaks at 443 nm for 4-PIMCFTPA and at 424 nm for 4-BICFTPA. Between the two fluorophores, 4-BICFTPA showed a blueshifted emission, unlike 4-PIMCFTPA, due to the supression of the π-conjugation and the twisting nature of the diphenylimidazole moiety. In addition, the obvious redshift in the PL spectra from solvent to solid [Figure 5 (right)] suggests the occurrence of strong intramolecular aggregation in the synthesized fluorophores [44]. However, the redshifted PL emission in the solid states of 4-BICFTPA might have been due to a change in the arrangement of the excited states [45], besides which the PL spectra of 4-BICFTPA showed a new peak at the tail due to the formation of an excimer in the solid states. Figure S16 shows the CIE color coordinates of the synthesized fluorophores, and Table S2 shows the resulting x and y color coordinates. Table S2 also indicates that the fluorophores showed deep-blue CIE coordinates. The absolute quantum yield (QY, Φ) of the newborn fluorophores was studied in both the solution phase and the solid phase. The blue emissive materials in the two phases showed good QYs (solution/solid of 82.7%/74.5%) for 4-PIMCFTPA and 68.7%/30.4% for 4-BICFTPA. A higher QY is essential for blue OLEDs (see Table 2) as it reduces the proportion of the non-radiative transition because of molecular interactions. The lower QY of 4-BICFTPA was observed due to the increase in the intramolecular vibration in the excited states as a result of the twisting conformation of 4-BICFTPA. On the contrary, 4-PIMCFTPA had a high rigid geometry, which reduced the non-radiative exciton and resulted in a high QY. The measured QYs and the digital images of the fluorophores are shown in Figures S18 and S19.

To further investigate the excited state properties of the synthesized fluorophores, the fluorescence lifetime was studied using the time-correlated single photon counting (TCSPC) technique under excitation with a suitable laser source. The decays of the lifetime are shown in Figure 6, and the resulting fluorescence lifetime data are summarized in Table 2. The decay curves were fit into the mono-exponential function, and the lifetime of the synthesized fluorophores were calculated as follows:

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

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
Table 2. Key photophysical properties of 4-PIMCFTPA and 4-BICFTPA.

| Compounds   | $T_g/T_d$ (°C) | Solution Abs$^c$ (nm) | Solution PL$^d$ (nm) | Solution τ$^f$ (ns) | Solution (%) | Solid (%) | $S_1^c$ (eV) | $T_1^c$ (eV) | Lifetime (τ) (ns) |
|-------------|---------------|-----------------------|-----------------------|---------------------|--------------|-----------|--------------|-------------|------------------|
| 4-PIMCFTPA  | 234/350       | 302, 356              | 443                   | 370                 | 426          | 82.7      | 74.5         | 3.19         | 2.59             | 1.87         |
| 4-BICFTPA   | 133/304       | 299, 341              | 424                   | 359                 | 433          | 68.7      | 30.4         | 3.08         | 2.40             | 1.85         |

$a$ Glass transition temperature. $b$ Thermal decomposition temperature corresponding to the 5% weight loss. $c$ Absorption maximum. $d$ Emission maximum. $e$ Singlet energy obtained from the onset-emission PL spectra. $f$ Triplet energy obtained from the 77K PL spectra.

Figure 4. Ultraviolet (UV) absorption spectra of the fluorophores in the dichloromethane (DCM) solution (left) and in the solid state (right).

Figure 5. Photoluminescence (PL) spectra of the fluorophores in the solution state (left) and the solid state (right).

$τ$ is the exponential decay time. The lifetime study was also performed for the fluorophores doped in the CBP host, and the results are shown in Figure S17. The emitters showed an enhanced lifetime when doped with 1 wt% in the CBP compared with their undoped states. The lifetime of the undoped 4-PIMCFTPA was 1.87 ns, and of the doped 4-PIMCFTPA, 2.40 ns. Similarly, 4-BICFTPA showed a lifetime of 1.85 ns when undoped, and 3.65 when doped.

4.3. Electrochemical properties

To understand the electrochemical characteristics of the fluorophores, cyclic voltammetry (CV) was performed using Bu$_4$NClO$_4$ (0.1 M) as the supporting electrolyte. Anhydrous dimethylformamide (DMF) was used as the medium, and the measurements were done at a scan rate of 100 mV s$^{-1}$. Figure 7 shows the cyclic voltammogram of the synthesized fluorophores, and Table 3 shows the
resulting electrochemical data. The fluorophores had distinct oxidation and reduction behaviors, which strongly indicates that they have bipolar charge carrier transport properties. The HOMO and LUMO energy levels were calculated using the following equations stated by de Leeuw et al. [46]:

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

The HOMO/LUMO energy levels of the fluorophores were \(-5.83/-2.84\) eV (4-PIMCFTPA) and \(-5.71/-2.67\) eV (4-BICFTPA) with energy bandgaps of 2.99 eV (4-PIMCFTPA) and 3.04 eV (4-BICFTPA). Among these two fluorophores, 4-BICFTPA showed a high electrical band gap, since its HOMO and LUMO were separated and distributed over the donor (triphenylamine) and the acceptor (diphenylimidazole), respectively, which allowed electronic transitions [47].

### 4.4. Electroluminescence properties

The above experimental study encouraged us to further explore the feasible applications of imidazole-triphenylamine-based fluorescent compounds in OLEDs. To further estimate the EL characteristics of a series of solution-processed multilayer undoped and doped OLEDs, we fabricated them with the energy levels and device structures shown in Figure 8. We fabricated two types of multilayer doped and undoped devices via the wet-process approach. The as-synthesized organic fluorophores were used as emitters and doped with different concentrations (1, 3, and 5 wt%) in a CBP host and in a pure dopant (100 wt%). First, undoped devices were fabricated with a device configuration of ITO (125 nm) / PEDOT: PSS (35 nm) / 4-PIMCFTPA or 4-BICFTPA (20 nm) / TPBi (40 nm) / LiF (1 nm) / Al (200 nm), as shown in Figure 8(a).

Poly(3,4-ethylenedioxythio-phene)-poly-(styrenesulfonate) (PEDOT:PSS) was incorporated as the hole-injection layer (HIL); 4,4’-Bis(N-carbazolyl)-1,1’-biphenyl (CBP), as the host material; and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi), as the
Figure 8. Schematic of the energy levels of the emitter materials doped/undoped in the host CBP for the fabrication of organic light-emitting diode (OLED) devices. (a) Pure film of the diphenylimidazole derivatives and (b) as dopant with the host CBP. Energy transfer routes from the host to the guest: (c) CBP:4-PIMCFTPA and (d) CBP:4-BICFTPA.

Electron-transporting layer (ETL) / hole-blocking layer (HBL). Lithium fluoride (LiF) and aluminum (Al) were used for the electron-injection layer (EIL) and the cathode, respectively. The cost-effective solution processing device fabrication approach was used to deposit the HIL and EML; and the thermal evaporation approach, to deposit other layers so as to achieve efficient performance of the devices. The current density–voltage–luminescence (J–V–L) characteristics and EL spectrum of all the fabricated doped and undoped OLED devices are shown in Figures 9 and 10, and their corresponding EL properties are listed in Table 4. The 4-PIMCFTPA-based fabricated undoped device had a high current density but comparatively low efficiencies, as shown in Figure 9. These can be related to exciton quenching, leakage of the charge carrier at the electrode interface, and aggregation, and could have resulted in a low-quality thin film. Despite that, the observed low efficiencies of the undoped OLED devices are ascribed to the occurrence of wider hole-injection barriers (<0.71–0.83 eV) between the HIL and the EML compared to the electron-injection barriers (<0.03–0.14 eV) that were used between the EML and the ETL, which can affect the charge carrier balance within the device structure. On the other hand, the 4-BICFTPA-based undoped device exhibited a high current density and lower brightness, along with better efficiencies, as shown in Figure 10. These results may be attributed to the reduced hole injection barrier (0.71 eV), which could have led to more majority charge carriers, i.e. holes, into the emissive zone. Furthermore, it has been reported that fluorescent emitters demonstrated improved performance when incorporated into an efficient host material [48,49].

A carbazole-based universal bipolar host, i.e. CBP, which has suitable HOMO–LUMO energy levels and a bipolar nature, was used in the doped devices to provide efficient charge-trapping by the fluorophore emitters. The doped devices were fabricated with the device configuration ITO (125 nm) / PEDOT: PSS (35 nm) / CBP: X wt% 4-PIMCFTPA or 4-BICFTPA (20 nm) / TPBi (40 nm) / LiF/Al.
Figure 9. Effects of the 4-PIMCFTPA doping concentration on the (a) luminance-voltage, (b) Current density – voltage, (c) power efficiency (PE) – luminance, (d) current efficiency (CE) – luminance, (e) luminance – current density, and (f) electroluminescence (EL) spectra using the CBP host with 1, 3, and 5 wt% dopant concentrations.

nm) / LiF (1 nm) / Al (200 nm), as shown in Figure 8(b), where X wt% refers to the 1, 3, and 5% concentrations of the emitters into the CBP host for the EML preparation. Considering the properties of emitters, CBP is a suitable host for generating efficient excitons and for transferring them to guest materials. Only singlet-to-singlet energy transfer takes place from the host to the guest via the forester resonance energy transfer (FRET) process. The triplet-to-singlet exciton transfer is inappropriate due to the huge difference in the energy levels of the host material, which limits the IQE to 25% and the external quantum efficiency to 5%. The 4-PIMCFTPA emitter-based devices showed high brightness, a low current density, and improved PE and CE, as shown in Figure 9, which can be related to (a) efficient energy transfer, (b) suitable matching of the HOMO–LUMO and triplet energy of the host with those of the dopants, (c) balanced charge-carriers in the recombination region, and (d) viability of the formation of radiative excitons. We note that the operating voltage decreased the brightness of the OLEDs because of the generation of the non-emissive excitons within the emissive layer [50]. We also observed that the current density of the 4-PIMCFTPA-based devices increased as their doping concentration increased from 1 to 3 wt% and decreased as their doping concentration increased from 3 to 5 wt%. This indicates that the EL properties are affected by the energy transfer from the host to the guest. The perfect alignment of the molecular energy levels of CBP and 4-PIMCFTPA might have caused the low turn-on and operating voltages [51].

The 4-BICFTPA emitter-based OLED devices displayed high brightness, low current density, and improved PE and CE, as shown in Figure 10. We observed that the current density of the 4-BICFTPA-based OLED devices increased as the doping concentration increased from 1 to 5 wt%, which may be attributed to the energy transfer from the host to the guest and the charge trapping effects in the EML. The increased current density enhanced the brightness of the devices as well as their performance in terms of CE and PE. Furthermore, the devices with 5 wt% 4-BICFTPA-doped OLED displayed higher current density and higher brightness, along with poorer performance, than the 1 and 3 wt% doped devices, perhaps due to charge imbalance and concentration quenching in the EML [52]. The devices with 5 wt% 4-BICFTPA-doped OLED also exhibited high turn-on and operating voltages, perhaps due to the difference in the frontier molecular orbital energy levels of the host and guest materials. This increased operating voltage has led to the poor performance of OLED devices [53].

The concluded electroluminescent properties of the 4-PIMCFTPA and 4-BICFTPA emitter-based deep-blue OLEDs have been incorporated in Table 4. The 1 wt% 4-PIMCFTPA-based OLED devices showed good EL properties with a PE of 0.3 lm W\(^{-1}\), a CE of 0.4 cd A\(^{-1}\), a
maximum luminescence of $417 \text{ cd/m}^2$, an EQE of 1.7%, and deep-blue CIE coordinates of $(0.17, 0.06)$, as listed in Table 4. At the 5 wt% doping concentration, the 4-PIMCFPTA-based device displayed the best performance in terms of a maximum PE of $1.7 \text{ lm/W}$, CE of $2.3 \text{ cd/A}$, and EQE of 1.8%, which may be attributed to the device’s better exciton utilisation efficiency (EUE) of 13.2% than the 2.2% of the 4-BICFTPA-based device, efficient charge balance into the emissive zone, and efficient forward energy transfer from the host to the guest [54]. On the other hand, the 3 wt% 4-BICFTPA emitter-doped device displayed a maximum PE of $0.1 \text{ lm/W}$, CE of $0.2 \text{ cd/A}$, and EQE of 0.3%, which are lower than those of the 4-PIMCFPTA emitter-based devices. This poor performance of the 4-BICFTPA emitter-based devices may be attributed to the lower measured singlet/triplet energy (-3.3 eV/-2.6 eV) levels of CBP compared to the singlet/triplet energy levels of 4-BICFTPA, which could have led to reverse energy transfer from the guest to the host [55]. The EL spectra of the devices are illustrated in Figures 9(f) and 10(f). For the undoped devices, a slight redshift was observed compared to the PL spectrum of the corresponding solid phase and those of the solution states. The redshift explicitly demonstrated the formation of aggregates in the solid phase, which would have induced crystallization by virtue of the more distorted conformations of the central TPA core and the peripheral imidazole moiety in the synthesized compounds. However, upon dilution with the host materials, the aggregation was restricted and thereby, the emission was regained. The 4-PIMCFPTA-based devices showed nearly pure deep-blue emissions with $\sim 400 \text{ nm}$ peaks.
and CIE coordinates of \( \gamma \sim 0.06 \). The CIE coordinates of the doped devices were similar to the standard pure deep-blue emission \((0.14, 0.08)\) determined by the NTSC.

In this study, we fabricated hole-only devices (HODs) and electron-only devices (EODs) to investigate the charge-carrier carrying capacities of the newly synthesized emitter materials. The HODs were made up of the following layers: ITO/PEDOT: PSS (35 nm) / TAPC (30 nm) / 4-PIMCFTPA or 4-BICFTPA (20 nm) / TAPC (30 nm) / Al (100 nm) [Figure S24 (a)], whereas the EODs were made up of the following layers: ITO/TPBi (35 nm) / 4-PIMCFTPA or 4-BICFTPA (20 nm) / TPBi [Figure S24 (b)]. To prevent electron and hole injection from the cathode and anode, respectively, TAPC and TPBi layers were utilized. Figure S24 shows the current density – voltage characteristic of the single-carrier devices. Surprisingly, the hole and electron current densities of the HODs and EODs with both compounds were almost equivalent, which confirmed their bipolar charge transport ability. The hole current density of the 4-PIMCFTPA-based device was higher, which indicates that 4-PIMCFTPA has a higher hole mobility than 4-BICFTPA, as shown in Figure S24 (c). We also found that the electron current density of the 4-BICFTPA-based device was slightly higher than that of the 4-PIMCFTPA-based device, which indicates that 4-BICFTPA has a higher electron mobility than 4-PIMCFTPA, as shown in Figure S24 (d).

5. Conclusion

Two novel deep-blue emitting donor-\( \pi \)-acceptor (D-\( \pi \)-A) fluorophores were successfully designed and synthesized by connecting hole-transporting triphenylamine (D) and electron-transporting phenothiazimidazole/diphenylimidazole (A) moieties with Ph-m-CF\(_3\) substitution at the N1 position of each imidazole using the cost-effective and easy solution-processed method. The fluorophores showed deep-blue emissions and a good QY in their solid and solution states, as well as good thermal stability. The fluorophores were used as dopant materials, and undoped and doped devices were fabricated. The undoped devices showed a deep-blue EL with a high current density and low brightness, unlike the doped devices. The OLED devices that were doped with the 4-PIMCFTPA fluorophore showed deep-blue emissions and high efficiencies: \( P_{\text{Fmax}} = 0.3 \) lm/W, \( C_{\text{Emax}} = 0.4 \) cd/A, and \( \text{EQE}_{\text{max}} = 1.7\% \), with CIE coordinates of \((0.17, 0.06)\) at a 1 wt% doping concentration. These results are very similar to those of the standard deep-blue emission coordinates \((0.14, 0.08)\) prescribed by the NTSC, as the \( \gamma \) value of these emitters was lower than the standard value.

Supporting information

General information is provided on the characterization and synthesis of the intermediates, the NMR spectra \((\text{\textsuperscript{1}H,} \text{\textsuperscript{13}C, and} \text{\textsuperscript{19}F NMR})\) and the mass spectra of the compounds, the CIE coordinates, the QYs of the compounds in the solution and solid phases, the calculated UV/Vis absorption spectra, the vertical transition composition, and the atom coordinates of the two investigated fluorophores.

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References

[1] C.W. Tang, and S.A. VanSlyke, Organic electroluminescent diodes, Appl. Phys. Lett. 51, 913–915 (1987). doi:10.1063/1.98799.

[2] Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, and W. Huang, Thermally activated delayed fluorescence materials towards the breakthrough of organoelectronics, Adv. Mater. 26, 7931–7958 (2014). doi:10.1002/adma.201402532.

[3] M. Zhu, and C. Yang, Blue fluorescent emitters: design tactics and applications in organic light-emitting diodes, Chem. Soc. Rev. 42, 4963–4976 (2013). doi:10.1039/C3CS35440G.Y.

[4] S.Y. Byun, J.H. Kim, D.R. Lee, C.S. Oh, K.S. Yook, and J.Y. Lee, Recent progress in high-efficiency blue-light-emitting materials for organic light-emitting diodes, Adv. Funct. Mater. 27, 1603007 (2017). doi:10.1002/adfm.201603007.

[5] J.E. Anthony, Functionalized acenes and heteroacenes for organic electronics, Chem. Rev. 106, 5028–5048 (2006). doi:10.1021/cr050966z.

[6] Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi, and M.P. Aldred, Recent advances in organic thermally activated delayed fluorescence materials, Chem. Soc. Rev. 46, 915–1016 (2017). doi:10.1039/C6CS00368K.

[7] G.B. Bodedla, K.R. Justin Thomas, M.-S. Fan, and K.-C. Ho, Benzimidazole-branched isomeric dyes: effect of molecular constitution on photophysical, electrochemical, and photovoltaic properties, J. Org. Chem. 81, 640–653 (2016). doi:10.1021/acs.joc.5b02590.

[8] J.C. Furgal, J.H. Jung, T. Goodson, and R.M. Laine, Analyzing structure–photophysical property relationships for isolated T8, T10, and T12 stilbenevinylsilsesquioxanes, J. Am. Chem. Soc. 135, 12259–12269 (2013). doi:10.1021/ja4043092.

[9] R.K. Konidena, K.R. Justin Thomas, S. Sahoo, D.K. Dubey, and J.-H. Jou, Multi-substituted deep-blue emitting carbazoles: a comparative study on photophysical and electroluminescence characteristics, J. Mater. Chem. C 5, 709–726 (2017). doi:10.1039/C6TC04870F.

[10] H. Sasabe, and J. Kido, Development of high performance OLEDs for general lighting, J. Mater. Chem. C 1, 1699–1707 (2013). doi:10.1039/C2TC00584K.

[11] Z. Peng, S. Tao, X. Zhang, J. Tang, C.S. Lee, and S.-T. Lee, New fluorene derivatives for blue electroluminescent devices: influence of substituents on thermal properties,
photoluminescence, and electroluminescence, J. Phys. Chem. C 112, 2165–2169 (2008). doi:10.1021/jp074834g.

[12] T.-L. Wu, H.-H. Chou, P.-Y. Huang, C.-H. Cheng, and R.-S. Liu, 3,6,9,12-tetrasubstituted chrysenes: synthesis, photophysical properties, and application as blue fluorescent OLED, J. Org. Chem. 79, 267–274 (2014). doi:10.1021/jo402429q.

[13] S. Thiery, C. Declaireix, D. Tondeliers, G. Seo, B. Gefroy, O. Jeanin, R. Métivier, J. Rault-Bertholot, and C. Poriel, 2-Substituted vs 4-substituted-9,9’-spirobi fluorone host materials for green and blue phosphorescent OLEDs: a structure–property relationship study, Tetrahedron 70, 6337–6351 (2014). doi:10.1016/j.tet.2014.05.081.

[14] H.-H. Chou, Y.-H. Chen, H.-P. Hsu, W.-H. Chang, Y.-H. Ouyang, X.-L. Li, L. Ai, D. Mi, Z. Ge, and S.-T.-L. Wu, H.-H. Chou, P.-Y. Huang, C.-H. Cheng, and X. Yang, B. Jiao, J.-S. Dang, Y. Sun, Y. Wu, G. Zhou, and W.-Y. Wong, Small-molecular blue phosphors for highly efficient electroluminescent devices, Adv. Mater. 24, 5867–5871 (2012). doi:10.1002/adma.201202222.

[15] X. Ouyang, X.-L. Li, L. Ai, D. Mi, Z. Ge, and S.-J. Su, Novel “hot exciton” blue phosphors for high performance fluorescent/phosphorescent hybrid white organic light-emitting diodes with superhigh phosphorescent dopant concentration and improved efficiency roll-off, ACS Appl. Mater. Interfaces 7, 7869–7877 (2015). doi:10.1021/acsami.5b081106.

[16] J.N. Moorthy, P. Venkatakrishnan, D.-F. Huang, and T.J. Chow, Blue light-emitting and hole-transporting amorphous molecular materials based on diarylaminophenyl-functionalized bismesitylenes, Chem. Commun. 2146–2148 (2008). doi:10.1039/B718250C.

[17] K.-H. Kim, S. Lee, C.-K. Moon, S.-Y. Kim, Y.-S. Park, J.-H. Lee, J. Woo Lee, J. Huh, Y. You, and J.-J. Kim, Phosphorescent dye-based supramolecules for high-efficiency organic light-emitting diodes, Nat. Commun. 5, 4769 (2014). doi:10.1038/ncomms5769.

[18] X. Yang, B. Jiao, J.-S. Dang, Y. Sun, Y. Wu, G. Zhou, and W.-Y. Wong, Achieving High-Performance Solution-Processed Orange OLEDs with the Phosphorescent Cyclometalated Trinuclear Pt(II) Complex, ACS Appl. Mater. Interfaces 10, 10227–10235 (2018). doi:10.1021/acsami.7b109172.

[19] Z. Chen, L. Wang, S. Su, X. Zheng, N. Zhu, C.-L. Ho, S. Chen, and W.-Y. Wong, Cyclometalated Iridium(III) Carbene Phosphors for Highly Efficient Blue Organic Light-Emitting Diodes, ACS Appl. Mater. Interfaces 9, 40497–40502 (2017). doi:10.1021/acsami.7b09172.

[20] B. Liu, F. Dang, Z. Feng, Z. Tian, J. Zhao, Y. Wu, X. Yang, G. Zhou, Z. Wu, and W.-Y. Wong, Novel iridium(iii) complexes bearing dimesitylboron groups with nearly 100% phosphorescent quantum yields for highly efficient organic light-emitting diodes, J. Mater. Chem. C 5, 7871–7883 (2017). doi:10.1039/C7TC02369C.

[21] C.-L. Ho, and W.-Y. Wong, Small-molecular blue phosphorescent dyes for organic light-emitting devices, New J. Chem. 37, 1665–1683 (2013). doi:10.1039/C3NJ00170A.

[22] S. Hirata, Y. Sakai, K. Masui, H. Tanaka, S.Y. Lee, H. Nomura, N. Nakamura, M. Yasumatu, H. Nakatani, Q. Zhang, K. Shizu, H. Miyazaki, and C. Adachi, Highly efficient blue electroluminescence based on thermally activated delayed fluorescence, Nat. Mater. 14, 330–336 (2015). doi:10.1038/nmat4154.

[23] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, Highly efficient organic light-emitting diodes from delayed fluorescence, Nature 492, 234–238 (2012). doi:10.1038/nature11687.

[24] Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka, and C. Adachi, Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence, Nat. Photonics 8, 326–332 (2014).

[25] N.C. Giebink, B.W. D’Andrade, M.S. Weaver, P.B. Mackenzie, J.J. Brown, M.E. Thompson, and S.R. Forrest, Intrins ic luminance in phosphorescent small-molecule organic light emitting devices due to bimolecular annihilation reactions, J. Appl. Phys. 103, 44509 (2008). doi:10.1063/1.2884530.

[26] R.J. Holmes, B.W. D’Andrade, S.R. Forrest, X. Ren, J. Li, and M.E. Thompson, Efficient, deep-blue organic electrophosphorescence by guest charge trapping, Appl. Phys. Lett. 83, 3818–3820 (2003). doi:10.1063/1.1624639.

[27] S. Thayumanavan, S. Barlow, and S.R. Marder, Synthesis of Unsymmetrical Triarylamines for Photonic Applications via One-Pot Palladium-Catalyzed Aminations, Chem. Mater. 9, 3231–3235 (1997). doi:10.1021/cm970567n.

[28] M. Taneda, K. Shizu, H. Tanaka, and C. Adachi, High efficiency thermally activated delayed fluorescence based on 1,3,5-tris-(4-diphenylaminophenyl)-2,4,6-tricyanobenzene, Chem. Commun. 51, 5028–5031 (2015). doi:10.1039/C5CC00511F.

[29] M. Liang, and J. Chen, Arylamine organic dyes for dyesensitized solar cells, Chem. Soc. Rev. 42, 3453–3488 (2013). doi:10.1039/C3CS35372A.

[30] S. Tao, L. Li, J. Yu, Y. Jiang, Y. Zhou, C.-S. Lee, S.-T. Lee, X. Zhang, and O. Kwon, Bipolar Molecule as an Excellent Hole-Transporter for Organic-Light Emitting Devices, Chem. Mater. 21, 1284–1287 (2009). doi:10.1021/cm803087c.

[31] W. Li, D. Liu, F. Shen, D. Ma, Z. Wang, T. Feng, Y. Xu, B. Yang, and Y. Ma, A Twisting Donor-Acceptor Molecule with an Intercrossed Excited State for Highly Efficient, Deep-Blue Electroluminescence, Adv. Funct. Mater. 22, 2797–2803 (2012). doi:10.1002/adfm.201200116.

[32] J. Tagare, H. Ulla, M.N. Satyanarayana, and S. Vaidyanathan, Efficient non-doped bluish-green organic light emitting devices based on N1 functionalized star-shaped phenanthroimidazole fluorophores, J. Photochem. Photobiol. A Chem. 353, 53–64 (2018). doi:10.1016/j.jphotochem.2017.11.001.

[33] J. Tagare, D.K. Dubey, J.-H. Jou, and S. Vaidyanathan, Near UV/deep-blue phenanthroimidazole-based luminophores for organic light-emitting diodes: experimental and theoretical investigation, ChemistrySelect 4, 6458–6468 (2019). doi:10.1002/selc.201900383.

[34] M.Y. Lai, C.H. Chen, W.S. Huang, J.T. Lin, T.H. Ke, L.Y. Chen, M.H. Tsai, and C.-C. Wu Benzi midazole/Amidine-Based Compounds Capable of Ambipolar Transport for Application in Single-Layer Blue-Emitting OLEDs and as Hosts for Phosphorescent Emitters, Angew. Chem. Int. Ed. 47, 581–585 (2008). doi:10.1002/ange.200704113.

[35] Y. Zhang, S.-L. Lai, Q.-X. Tong, M.-F. Lo, T.-W. Ng, M.-Y. Chan, Z.-C. Wen, J. He, K.-S. Jeff, X.-L. Tang, W.-M. Liu,
J. Tagare, D.K. Dubey, J.-H. Jou, and S. Vaidyanathan, Synthesis, photophysical, theoretical and electroluminescence study of triphenylamine-imidazole based blue fluorophores for solution-processed organic light emitting diodes, Dye. Pigment 160, 944–956 (2019). doi:10.1016/j.dyepig.2018.09.007.

J. Tagare, D.K. Dubey, R.A.K. Yadav, J.-H. Jou, and S. Vaidyanathan, Triphenylamine-imidazole-based luminophores for deep-blue organic light-emitting diodes: experimental and theoretical investigations, Mater. Adv. 1, 666–679 (2020). doi:10.1039/D0MA00007H.

Frisch MJ, et al. Gaussian 09, revision D01. (Wallingford, CT, Gaussian, Inc.; 2009). A. Ivanauskaite, R. Lygaitis, S. Raisys, K. Kazlauskas, G. Kreiza, D. Volyniuk, D. Gudeika, S. Jursenas, and J. V Grazulevicius, Structure–property relationship of blue solid state emissive phenanthroimidazole derivatives, Phys. Chem. Phys. 19, 16737–16748 (2017). doi:10.1039/C7CP02248D.

J. Tagare, R. Boddula, S.S. Sudheendran, D.K. Dubey, J.-H. Jou, S. Patel, and S. Vaidyanathan, Efficient near ultraviolet emission (CIE $\ell_u$: 0.06) organic light-emitting diodes based on phenanthroimidazole–alkyl spacer–carbazole fluorophores: experimental and theoretical investigation, J. Mater. Chem. C 8, 16834–16844 (2020). doi:10.1039/D0TC3720F.

Z. Ge, T. Hayakawa, S. Ando, M. Ueda, T. Akiike, H. Miyamoto, T. Kajita, and M. Kakimoto, Spin-Coated Highly Efficient Phosphorescent Organic Light-Emitting Diodes Based on Bipolar Triphenylamine-Benzimidazole Derivatives, Adv. Funct. Mater. 18, 584–590 (2008). doi:10.1002/adfm.200700913.

Z. Ge, T. Hayakawa, S. Ando, M. Ueda, T. Akiike, H. Miyamoto, T. Kajita, and M. Kakimoto, Solution-Processible Bipolar Triphenylamine-Benzimidazole Derivatives for Highly Efficient Single-Layer Organic Light-Emitting Diodes, Chem. Mater. 20, 2532–2537 (2008). doi:10.1021/cm7035458.

F.-M. Hsu, C.-H. Chien, C.-F. Shu, C.-H. Lai, C.-C. Hsieh, K.-W. Wang, and P.-T. Chou, A Bipolar Host Material Containing Triphenylamine and Diphenylphosphoryl-Substituted Fluorene Units for Highly Efficient Blue Electrophosphorescence, Adv. Funct. Mater. 19, 2834–2843 (2009). doi:10.1002/adfm.200900703.

J. Jayabhathari, V. Thanikachalam, and G.A. Sundari, Efficient electroluminescent hybridized local and charge-transfer host materials with small singlet–triplet splitting to enhance exciton utilization efficiency: excited state transition configuration, RSC Adv. 9, 6658–6660 (2019). doi:10.1039/C9RA00135B.

Y.-S. Park, S. Lee, K.-H. Kim, S.-Y. Kim, J.-H. Lee, and J.-J. Kim, Exciplex-forming co-host for organic light-emitting diodes with ultimate efficiency, Adv. Funct. Mater. 23, 4914–4920 (2013). doi:10.1002/adfm.201300547.

C.-J. Kuo, T.-Y. Li, C.-C. Lien, C.-H. Liu, F.-I. Wu, and M.-J. Huang, Bis(phenanthroimidazolyl)bisphenyl derivatives as saturated blue emitters for electroluminescent devices, J. Mater. Chem. 19, 1865–1871 (2009). doi:10.1039/B816327H.

D.M.de Leeuw, M.M.J. Simonen, A.R. Brown, and R.E.F. Einerhand, Stability of n-type doped conducting polymers and consequences for polymeric microelectronic devices, Synth. Met. 87, 53–59 (1997). doi:10.1016/S0379-6779(97)80097-5.

D. Hu, F. Shen, H. Liu, P. Lu, Y. Lv, D. Liu, and Y. Ma, Separation of electrical and optical energy gaps for constructing bipolar organic wide bandgap materials, Chem. Commun. 48, 3015–3017 (2012). doi:10.1039/C2CC17682C.

J.-H. Jou, S. Kumar, P.-H. Fang, A. Venkateswararao, K.R.J. Thomas, J.-I. Shuye, Y.-C. Wang, T.-H. Li, and H.-H. Yu, Highly efficient ultra-deep blue organic light-emitting diodes with a wet- and dry-process feasible cyanofluorene acetylene based emitter, J. Mater. Chem. C 3, 2182–2194 (2015). doi:10.1039/C4TC02547D.

A. Sharma, R. Balasaravanavan, K.R.J. Thomas, M. Ram, D.K. Dubey, R.A.K. Yadav, and J.-H. Jou, Tuning photophysical and electroluminescent properties of phenanthroimidazole decorated carbazoles with donor and acceptor units: beneficial role of cyano substitution, Dye. Pigment 184, 108830 (2021). doi:10.1016/j.dyepig.2020.108830.

A. Sharma, D. Saklani, K.R. Justin Thomas, Shahnawaz, S. Swayamprabha, J.-H. Jou, Synthesis and characterization of multi-substituted carbazole derivatives exhibiting aggregation-induced emission for OLED applications, Org. Electron. 86 (2021) 105864. doi:10.1016/j.orgel.2020.105864.

J. Tagare, R.A.K. Yadav, S.S. Swayamprabha, D.K. Dubey, J.-H. Jou, and S. Vaidyanathan, Efficient solution-processed deep-blue CIE $\ell_y \in (0.05)$ and pure-white CIE $\ell_x,\ell_y \in (0.34, 0.32)$ organic light-emitting diodes: experimental and theoretical investigation, J. Mater. Chem. C 3, 2182–2194 (2015). doi:10.1039/D1TC00228G.

A. Sharma, R. Balasaravanavan, K.R.J. Thomas, M. Ram, D.K. Dubey, R.A.K. Yadav, and J.-H. Jou, Tuning photophysical and electroluminescent properties of phenanthroimidazole decorated carbazoles with donor and acceptor units: beneficial role of cyano substitution, Dye. Pigment 184, 108830 (2021). doi:10.1016/j.dyepig.2020.108830.

A. Salehi, C. Dong, D.-H. Shin, L. Zhu, C. Papa, A. Thy Bui, F.N. Castellano, and F. So, Realization of high-efficiency fluorescent organic light-emitting diodes with low driving voltage, Nat. Commun. 10, 2305 (2019). doi:10.1038/s41467-019-10260-7.

J. Luo, G. Xie, S. Gong, T. Chen, and C. Yang, Creating a thermally activated delayed fluorescence channel in a single polymer system to enhance exciton utilization efficiency for bluish-green electroluminescence, Chem. Commun. 52, 2292–2295 (2016). doi:10.1039/C5CC09797E.

B.S.B. Karunathilaka, U. Balijapalli, C.A.M. Seneviratne, S. Yoshida, Y. Esaki, K. Goushi, T. Matsushima, A.S.D. Sandanayaka, and C. Adachi, Suppression of external quantum efficiency rolloff in organic light-emitting diodes by scavenging triplet excitons, Nat. Commun. 11, 4926 (2020). doi:10.1038/s41467-020-18292-0.