Exciplex Electroluminescence Induced by Cross-Linked Hole-Transporting Materials for White Light Polymer Light-Emitting Diodes

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ABSTRACT: A new class of cross-linkable N,N,N′,N′-tetraphenyl-1,1′-biphenyl-4,4′-diamine (TPD)-based hole-transporting materials (HTMs), DV-OMe-TPD, DV-Me-TPD, and DV-F-TPD, were designed and synthesized. Two vinyl groups in the TPD units are used for thermal cross-linking, whereas methoxy, methyl and fluoro groups are introduced to modulate the HOMO energy levels of the HTMs. These HTMs are thermally cross-linked to overcome interfacial mixing, realizing solution-processed polyfluorene (PFO)-based devices (ITO/cross-linked HTMs/PFO/CsF/Al). Besides the characteristic blue emission of PFO, the devices exhibited a red emission whose energy is highly dependent on the HOMO energy of the cross-linked HTM used in the device. This result suggests that the red electroluminescence is derived from the exciplex generated by the adjacent hole and electron at the cross-linked HTM/fluorenone heterojunction interface. By doping small amount of 4,7-bis(9,9-dihexylfluorene-2-yl)-2,1,3-benzothiadiazole (BFBT) into the emissive layer (EML) to compensate green emission, the devices with the configuration of ITO/PEDOT:PSS/DV-Me-TPD/PFO doped with BFBT/CsF/Al exhibited white electroluminescence comprising three primary colors simultaneously. The 0.04 wt % doped device achieved a maximum luminous efficiency of 5.28 cd/A, which represents the highest efficiency for WPLEDs reported so far on the basis of the exciplex strategy. This device showed CIE chromaticity coordinates of (0.32, 0.42) which are close to the ideal white point (0.33, 0.33). We have demonstrated that integrating cross-linked triarylamine-based HTMs with fluorenone defects in PFO to induce exciplex electroluminescence can provide a useful way for realizing WPLED devices.

INTRODUCTION

White light-emitting diodes (WLEDs) have received considerable interest due to their potential applications in full color flat panel displays, back-lighting sources for liquid-crystal displays, and solid-state lighting sources.1 White polymer light-emitting diodes (WLEDs) are particularly promising, because polymer-based devices possess several advantages such as low cost, flexibility and large area by solution processing.2 A ideal white PLED is characterized by an emission that covers the full spectral range of the visible region (380–780 nm) and a Commission International d’Eclairage (CIE) chromaticity coordinates of (0.33, 0.33). To create white-light emission, the most straightforward way is to mix three components which can independently emit three primary colors (red, green, and blue). Several strategies have been implemented to realize WPLEDs by blending three emitting components such as polymer blends3 or polymers doped with small molecules.4 However, severe phase separation or undesired energy transfer between different components are critical issues to control the color composition.5 Single-polymer systems with different chromophoric groups on the main chain or side chain have been reported to address this problem.6 It is highly desirable to develop other emissive systems that can reduce the number of emissive components to achieve white light electroluminescence.

To achieve high-performance LEDs devices, triarylamine-based hole transporting layers (HTL) are widely incorporated into multilayer devices to improve the hole transporting properties.7 Because of their relatively high-lying LUMO energy levels, these HTLs also function as effective electron-blocking layers to confine electrons in the emissive layer (EML) near the interface with HTL. When the electron and hole recombine in the EML, exciton emission with pure emissive band will be observed. If the electron is confined in the EML, while the hole is still located in the HTL, the transient bimolecular excited state, also termed as exciplex, can be formed by adjacent hole and electron at the HTL/EML heterojunction interface.8 Exciplex usually results in a characteristic broad and structureless emission. In addition, compared to the exciton emission coming from a single species (i.e., EML or HTL material), the exciplex emission is bathochromically shifted to the longer wavelengths, because its energy is associated with the energy offset between the HOMO of the HTL material and the LUMO of the EML material. The occurrence of the undesired exciplex emission is detrimental to a PLED device that requires single-color...
illumination. However, if this additional emission can be smartly controlled and utilized, it may provide a suitable red-light emission in the visible region for WPLED. Modulating electronic properties of the hole-transporting material affords a promising way to tailor the exciplex characteristics and its emission. Nevertheless, bilayer exciplex emission at HTL/EML interface is not well exploited for polymer-based WLEDs, and the performance based on this strategy in the literatures is still limited. The major obstacle to hinder this direction is that the bottom hole-transporting layer will be eroded by the solvent used in the subsequent spin-coating to deposit the emissive layer.

In this case, hole will be trapped at interfacial mixing zone near the heterojunction. Therefore, incorporation of various hole-transporting materials to realize WPLEDs by exciplex strategy is technologically difficult. Until now, only poly(vinyl carbazole) (PVK) having certain solvent resistance represents the most commonly used HTM for multilayer devices. Jen and co-workers have reported a series of triarylamine-based hole-transporting materials attaching two additional styrene groups for thermal cross-linking. Two vinyl groups are directly introduced on the two phenyl rings in the TPD unit, forming two styrene groups to serve as the cross-linkers. This molecular design creates the most compact HTM hybridizing TPD and styrene units together, which significantly increases the weight content of active TPD unit. Moreover, in order to fine-tune the electronic properties of HTMs, the para position of the other two phenyl rings in the TPD is further introduced with strong electron-donating methoxy groups (denoted as DV-OMe-TPD), weak electron-donating methyl group (denoted as DV-Me-TPD) and electron-withdrawing group (denoted as DV-F-TPD). Their molecular structure is shown in Scheme 1.

Polyfluorenes (PFO) have been demonstrated as a good candidate for blue PLEDs because of their high photoluminescence (PL) quantum efficiency. However, the blue-light emitting devices based on homopolymer PFO suffer from the poor color stability due to the formation of fluorenone defects. It is envisaged that this unwanted fluorenone impurity in PFO for blue PLEDs can become utilizable for WPLEDs. On the basis of the newly designed cross-linkable HTMs toward WPLEDs in this
research, PFO is used to serve as the host to produce the blue emission, while the green emission is generated from a guest material, 4,7-bis(9,9-dihexylfluoren-2-yl)-1,3-benzothiadiazole (BFBT),6c doped into the EML (Scheme 1). The red emission comes from the exciplex formed at the interface between the cross-linked TPD-based molecule and the fluorenone species. By tuning the amount of BFBT, we have achieved white electroluminescence comprising the three primary colors simultaneously by blending only two components in the EML. Combining fluorenone defects in PFO with cross-linked HTMs to induce exciplex emission may afford an easy and useful strategy to achieve WPLEDs.

**RESULTS AND DISCUSSION**

**Synthesis of Materials.** The synthesis of these cross-linkable hole transporting materials are shown in Scheme 2. By utilizing Ullmann coupling, N,N'-diphenylbenzidine 1 was coupled with 2 equiv of 4-iodotoluene and 4-methoxyiodobenzene to yield TPD-based compound 3a and 3b, respectively, whereas 3c was obtained by reacting 1 with 1-fluoro-4-iodobenzene by Hartwig–Buchwald palladium-catalyzed amination. Vilsmeier formlylation of compound 3 with 2 equiv of phosphorus oxychloride (POCl3) and N,N-dimethylformamide (DMF) to yield compound 4 after hydrolysis. Finally, the two formyl groups in the compound 4 were converted into two vinyl groups by using Wittig reaction to yield the corresponding cross-linkable HTMs DV-Me-TPD, DV-OMe-TPD, and DV-F-TPD.

**Thermal Properties and Cross-Linking Conditions.** The decomposition temperature ($T_d$) of the HTMs was determined by thermogravimetric analysis (TGA). All the HTMs showed high thermal stability with $T_d$ ranging from 448 to 462 °C (Table 1). Differential scanning calorimetry (DSC) was used to investigate the thermal and cross-linking properties of these HTMs (Figure 1). In the first scan of DSC, all of the HTMs showed a board exothermic peak which is unambiguously indicative of the occurrence of cross-linking of styrene groups. It is noteworthy that the maximum exothermic temperature $T_c$ follows the trend: DV-F-TPD (106 °C) < DV-Me-TPD (147 °C) < DV-OMe-TPD (168 °C). It has been generally accepted that two styrene groups undergo Diels–Alder dimerization followed by hydrogen radical transfer to generate the benzylic radical that initiates the vinyl radical polymerization.14 The stability of benzylic radical intermediate will determine how easily the thermal cross-linking can occur. We propose that the electron-withdrawing ability of the para fluoro group reduces the electron density of nitrogen, thus improving the stability of benzylic radical, whereas methoxy group may decrease the radical stability. This electronic effect also permits us to fine-tune the cross-linking temperatures in the solid state. To prepare the thin film of these HTMs, 1.0 wt % chlorobenzene solutions of the HTMs were spin-coated onto the ITO substrate. On the basis of the DSC studies, we employed an isothermal heating at 180 °C for 30 min under nitrogen atmosphere to ensure complete cross-linking for all the HTMs.

**Optical Properties and Solvent Resistance.** The UV–vis absorption spectra of these HTMs in the solid film are shown in Figure S1 in the Supporting Information. DV-OMe-TPD showed the most red-shifted absorption maximum at 377 nm, whereas DV-F-TPD exhibited the most blue-shifted absorption maximum at 367 nm (Table 1). This can be rationalized by the fact that the electron-donating methoxy group raises the HOMO energy level, whereas the withdrawing fluoro group will lower the HOMO energy level. Compared with the uncross-linked HTMs in the solid state, the absorption maxima of the cross-linked HTMs are slightly blue-shifted presumably due to the disrupted coplanarity of TPD molecule after the covalent bonds are formed intermolecularly (Figure S1, Supporting Information). The resultant films are very transparent and absorb mainly in the UV region so it causes very little interference with the light generated from the device.

**Table 1. Physical Properties of the HTMs**

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$T_d$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\lambda_{max}$ (nm) $^a$</th>
<th>$\lambda_{max}$ (nm) $^b$</th>
<th>HOMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DV-TPD-OMe</td>
<td>448</td>
<td>168</td>
<td>377</td>
<td>363</td>
<td>-5.10</td>
<td>3.00</td>
<td>-2.10</td>
</tr>
<tr>
<td>DV-TPD-Me</td>
<td>462</td>
<td>147</td>
<td>372</td>
<td>359</td>
<td>-5.20</td>
<td>3.02</td>
<td>-2.18</td>
</tr>
<tr>
<td>DV-TPD-F</td>
<td>454</td>
<td>106</td>
<td>367</td>
<td>351</td>
<td>-5.34</td>
<td>3.05</td>
<td>-2.29</td>
</tr>
</tbody>
</table>

$^a T_d$ is the decomposition temperature determined by TGA at 5% weight loss. $^b T_c$ is the temperature of maximum exothermic peak obtained from DSC. $^c$ The wavelength of maximum absorption before cross-linking of HTMs. $^d$ The wavelength of maximum absorption of HTMs after cross-linking. $^e$ HOMO energy level was calculated by CV using ferrocene value of -4.8 eV below the vacuum level. $^f E_g$ is the optical band gap. $^g$ LUMO = HOMO + $E_g$.

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Figure 1. First heating (a) and second heating (b) of DSC measurements of the HTMs with a heating rate of 10 °C/min.
Solvent resistance of the cross-linked HTMs was investigated by monitoring UV–vis spectra. As shown in Figure 2, the absorption intensity of the cross-linked DV-Me-TPD remains almost unchanged before and after rinsing with chlorobenzene (a good solvent for both precursor monomers and polyfluorene), indicating the sufficient solvent resistance has been generated. Similar phenomena were observed for DV-OMe-TPD and DV-F-TPD.

Furthermore, we employed Infrared spectroscopy to monitor the functional groups transformation. The vibrational stretching of the vinyl groups at 1627 cm⁻¹ in DV-Me-TPD almost disappear after curing at 180 °C for 30 min, confirming that the solvent resistance comes from the cross-linking of the styryl groups (Figure S2, Supporting Information).

The surface roughness of the HTMs spin-coated on ITO was examined by atomic force microscopy (AFM) before and after thermal curing at 180 °C for 30 min (Figure S3, Supporting Information). Although these HTMs are small molecules, smooth and uniform thin films could be observed for each sample over a 2 × 2 μm scan area, and the root-mean-square (rms) surface roughness for DV-Me-TPD, DV-F-TPD, and DV-OMe-TPD is 0.37, 0.45, and 0.34 nm, respectively. After cross-linking, the surface roughness increased to 1.15, 1.00, and 0.97 nm for cross-linked DV-Me-TPD, DV-F-TPD, and DV-OMe-TPD, respectively. These results indicated that these small-molecule-based HTMs can have good film-forming properties.

**Electrochemical Properties.** Cyclic voltammetry (CV) was used to investigate the electrochemical properties of these hole transporting materials after these HTMs were cured at 180 °C for 30 min on the ITO (Figure 3). The highest occupied molecular orbital (HOMO) energy levels of these HTMs were estimated from the onset of oxidation potential using ferrocene/ferrocenium as standard, while the lowest unoccupied molecular orbital (LUMO) levels were estimated from the difference between the HOMO energy level and the optical band gap measured from absorption spectrum. Because the fluoro group with electron-withdrawing ability reduces the electron density of nitrogen, DV-F-TPD becomes more difficult to be oxidized and thus shows the lowest-lying HOMO energy level of −5.34 eV. As the electron-donating power of the substituent increases to strengthen the nitrogen electron density, the HOMO energy level gradually decreases to −5.20 eV for DV-Me-TPD and −5.10 eV for DV-OMe-TPD, respectively.

**Device Performance.** To estimate the intrinsic hole mobilities of these cross-linked HTMs, hole-only devices (ITO/PEDOT:PSS/cross-linked HTMs/Au) were first fabricated by means of the space-charge limit current (SCLC) theory. The device based on DV-F-TPD, DV-Me-TPD, and DV-OMe-TPD exhibited the comparable hole mobilities of 7.2 × 10⁻⁶ cm²/V s, 6.2 × 10⁻⁴ cm²/V s, and 3.4 × 10⁻⁴ cm²/V s, respectively. To further investigate the hole-transporting properties of these new materials, we fabricated the devices with the configuration ITO/cross-linked HTMs/PFO/CsF/Al where PFO was employed as the blue emitting layer. The brightness-voltage (L–V) and luminous efficiency–current density characteristics of the device are shown in Figure 4 and Figure 5, respectively. Table 2 lists the device parameters. Compared to the devices with DV-F-TPD and DV-OMe-TPD as HTL, the device based on DV-Me-TPD exhibited the highest performance in terms of the lower operational voltage, higher maximum luminous efficiency (1.3 cd/A), and higher maximum brightness (2586 cd/m² at 15.5 V). Because the three HTMs have very similar molecular structures, the variations in device performance are presumably ascribed to the difference in HOMO energy levels. The work function of the ITO and the HOMO level of the PFO are located at −4.8 eV and −5.8 eV, respectively. The results suggest that DV-Me-TPD with the HOMO energy at −5.2 eV serves as the most suitable energy intermediate to provide a cascade hole-transporting
pathway which allows for more balanced charge carriers in the devices. Raising (DV-OMe-TPD) or lowering (DV-F-TPD) the HOMO levels will also increase the energy barriers at DV-OMe-TPD/PFO (0.7 eV) or ITO/DV-TPD (0.54 eV) interfaces, respectively, thus resulting in unbalanced charge transportation and lower device performance. It should be noted that the devices incorporating these HTMs show much improved performance compared to a control device (ITO/PEDOT:PSS/PFO/CsF/Al) using PEDOT:PSS as hole-injection layer. The maximum luminous efficiency of the device with DV-Me-TPD is about 4 times higher than that of the device using PEDOT:PSS. This pronounced improvement in device performance is due to the balanced charge injection and transporting characters, leading to the effective charge recombination within the emitting layer.

In addition to the characteristic emission of PFO from 400 to 500 nm being observed in the electroluminescent spectra, the devices incorporating these cross-linked HTMs also showed a broad emission covering from 550 to 700 nm (Figure 6). It has been known that, under the thermal and electrical field circumstances, fluorene moieties in the PFO are prone to be oxidized to fluorenone species. We speculate that this red emission may come from the exciplex at the interface between the fluorenone defects and HTL. Fortunately, these HTMs having different HOMO energy levels allow us to specifically investigate the origin of the red emission. It was found that the energy gap of 2.0 eV between the HOMO level of DV-OMe-TPD (−5.1 eV) and the LUMO level of fluorenone (−3.1 eV) perfectly matches the energy of the red emission band ($\lambda_{\text{max}} = 620$ nm) in DV-OMe-TPD-based device. This implies that the formation of fluorenone/DV-OMe-TPD exciplex at the interface is responsible for the red emission. Furthermore, when DV-Me-TPD and DV-F-TPD with the lower-lying HOMO energy levels are used to increase the energy gap at the interface, the emission maximum wavelength is shifted to 609 and 596 nm, respectively. The HOMO-dependent electroluminescence confirms the emission is derived from the exciplex emission. The energy diagram and the exciplex mechanism in the device are shown in Figure 7.

To further optimize the performance of DV-Me-TPD-based device, hole injection PEDOT:PSS was inserted in the device with the configuration of ITO/PEDOT:PSS/DV-Me-TPD/PFO/CsF/Al. Curing at a moderate temperature of 180 °C for 30 min allows for cross-linking of DV-Me-TPD layer without degrading the bottom PEDOT:PSS layer. As expected, the incorporation of PEDOT:PSS layer further enhances the device performance with a maximum luminance efficiency of 1.53 cd/A, maximum brightness of 3245 cd/m² and a lower turn-on voltage (Figures 4 and 5). The DV-Me-TPD layer has the HOMO levels at −5.2 eV, which is in between those of PEDOT:PSS (−5.0 eV) and PFO (−5.8 eV). Therefore, the PEDOT:PSS/DV-Me-TPD double layer provides an energy-matched cascade hole-injecting/transporting pathway leading to more balanced charge flux in the devices. The EL spectrum of PEDOT:PSS/DV-Me-TPD-based device also displays an exciplex emission, which is consistent with the devices without PEDOT:PSS layer.

Despite that the exciplex-induced red emission is detrimental to the PFO-based blue emitting devices, we envision that the dual

Table 2. Electroluminescence Data of Devices Based on the Structure (ITO/HTMs/PFO/CsF/Al)

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$B^a$ (cd/m²)</th>
<th>LE$^a$ (cd/A)</th>
<th>$B_{\text{max}}$ (cd/m²)</th>
<th>LE$^\text{max}$ (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>39 (at 7.5 V)</td>
<td>0.19</td>
<td>1071 (at 10.5 V)</td>
<td>0.28</td>
</tr>
<tr>
<td>DV-OMe-TPD</td>
<td>161 (at 12.7 V)</td>
<td>0.79</td>
<td>1138 (at 17 V)</td>
<td>0.87</td>
</tr>
<tr>
<td>DV-F-TPD</td>
<td>148 (at 11.4 V)</td>
<td>0.73</td>
<td>2011 (at 15.5 V)</td>
<td>0.89</td>
</tr>
<tr>
<td>DV-Me-TPD</td>
<td>250 (at 12 V)</td>
<td>1.24</td>
<td>2586 (at 15.5 V)</td>
<td>1.30</td>
</tr>
<tr>
<td>PEDOT:PSS/DV-Me-TPD</td>
<td>282 (at 10.7 V)</td>
<td>1.39</td>
<td>3245 (at 14 V)</td>
<td>1.53</td>
</tr>
</tbody>
</table>

$^a$ Recorded at 20 mA/cm².
emission could be smartly utilized to realize white emitting PLED, if a green emitting source is incorporated in EML. In this regard, we fabricated the devices with the configuration ITO/PEDOT/PVDF-Me-TPD/PFO: X wt % of BFBT/CsF/Al where BFBT is a green emitting dopant in the emissive layer (Scheme 1). By doping small amount of BFBT (0.02, 0.04, and 0.08 wt %) to control energy transfer in the EML, the intensity of three primary colors can be carefully adjusted toward ideal white-light electroluminescence. Table 3 summarizes the characteristics of the white-emitting devices. Indeed, all the devices exhibited electroluminescence covering the entire visible window (400–800 nm) with three major peaks centered at ca. 450, 518, and 610 nm. The blue region is the characteristic emission of the PFO host, while the green and red emissions come from the BFBT dopant and the fluorenone/PVDF-Me-TPD exciplex, respectively. The Commission Internationale d’Enclairage (CIE) chromaticity coordinates were evaluated to determine the color composition of the devices. The 0.02 wt % concentration of BFBT is too low to provide enough green light intensity. Thus, the corresponding device exhibited CIE chromaticity coordinates at (0.25, 0.28) at a bias of 9 V. However, by increasing the BFBT content, the CIE chromaticity coordinates were shifted to (0.32, 0.42) for the 0.04 wt % doped device and (0.32, 0.44) for 0.08 wt % doped device respectively, which are very close to the ideal white point (0.33, 0.33) (Figure 8). Figures 9 and 10 display the voltage—brightness (V–B) curves and luminous efficiency—current density of the white-emitting devices. As the doping content of BFBT increases from 0.02 to 0.04 and 0.08 wt %, the brightness and the luminous efficiency gradually increases, whereas the operation voltage is reduced. The 0.04 wt % doped white-emitting device showed a maximum luminance efficiency of 5.28 cd/A. To our knowledge, this value represents the highest among the exciplex-based white-emitting PLEDs.

**CONCLUSIONS**

Blue-emitting devices based on PFO suffer from poor color stability due to the formation of fluorenone defects. Utilization of fluorenone defects in PFO to induce exciplex emission may afford a useful strategy to achieve WPLED devices. Successful integration of triarylamine-based hole-transporting material into multilayer device plays a key role for exciplex formation at the HTL/EML interface. For this purpose, a new class of cross-linkable TPD-based HTMs, DV-Ome-TPD, DV-Me-TPD, and DV-F-TPD, were designed and synthesized. Two vinyl groups introduced on the two phenyl rings in the TPD unit are used as the cross-linkers, whereas methoxy, methyl and fluoro groups are incorporated to modulate the HOMO energy levels of the HTMs. After cross-linking under mild thermal polymerization, the HTL with solvent resistance can overcome interfacial mixing, allowing us to successfully fabricate the polyfluorene-based devices with configuration of ITO/cross-linked HTMs/PFO/CsF/Al.

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**Table 3. Performance of the Devices ITO/PEDOT:PSS/DV-Me-TPD/PFO:X wt % BFBT/CsF/Al**

<table>
<thead>
<tr>
<th>BFBT (wt %)</th>
<th>B (cd/m²)</th>
<th>LE (cd/A)</th>
<th>B_max (cd/m²)</th>
<th>LE_max (cd/A)</th>
<th>CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>570 (at 10.3 V)</td>
<td>2.90</td>
<td>4991 (at 18 V)</td>
<td>4.16</td>
<td>(0.25, 0.28)</td>
</tr>
<tr>
<td>0.04</td>
<td>619 (at 10.6 V)</td>
<td>3.11</td>
<td>3125 (at 17 V)</td>
<td>5.28</td>
<td>(0.32, 0.42)</td>
</tr>
<tr>
<td>0.08</td>
<td>672 (at 9.6 V)</td>
<td>3.49</td>
<td>4388 (at 16 V)</td>
<td>5.21</td>
<td>(0.32, 0.44)</td>
</tr>
</tbody>
</table>

a Recorded at 20 mA/cm². b Recorded at 9 V.
In addition to the characteristic blue emission of PFO, the devices exhibited a red emission covering from 550 to 700 nm. The maximum wavelength of the red emission is correlated with the HOMO energy of the cross-linked HTM used in the device, suggesting that the red emission is derived from the exciplex formed by the adjacent hole and electron at the cross-linked HTM/fluorenone heterojunction interface. By doping small amounts of BFBT into EML to compensate green emission, the devices with the configuration of ITO/PEDOT/DV-Me-TPD/PFO doped with BFBT/CsF/Al exhibited white electroluminescence comprising the three primary colors simultaneously. The 0.04 wt % doped device achieved a maximum luminous efficiency of 5.28 cd/A which represents the highest efficiency for WPLEDs based on the exciplex strategy. This device also showed CIE chromaticity coordinates of (0.32, 0.42) which are close to the ideal white point (0.33, 0.33).

**EXPERIMENTAL SECTION**

**General Measurement and Characterization.** All chemicals, unless specified, were purchased from Aldrich, TCI, and Acros and used as received. The $^1$H and $^{13}$C NMR spectra were collected on a Varian Unity-300 spectrometer operating at 300 and 75 MHz in deuterated chloroform solution and using tetramethylsilane as reference. The IR spectra were collected using the PerkinElmer Spectrum One FT-IR spectrometer and these HTMs solutions were dropped on the homemade KBr film for study. Cyclic voltammetric data were performed on an Autolab ADC 164 using a conventional three-electrode cell with an ITO electrode, and a saturated calomel electrode as the reference electrode.

**Synthesis of 3a.** To a two-necked flask were added Cu (10.34 g, 83.4 mmol), 4-iodoanisole (1.76 g, 53%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.37 (s, 6 H), 7.05 ($d$, $J$ = 8.4 Hz, 4 H), 7.10 ($d$, $J$ = 8.4 Hz, 4 H), 7.17–7.23 (m, 8 H), 7.53 ($d$, $J$ = 8.1 Hz, 4 H), 7.68 ($d$, $J$ = 8.7 Hz, 4 H), 9.81 (s, 2 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 21.1, 119.5, 126.2, 127.3, 127.5, 129.4, 134.3, 140.9, 147.2, 148.3, 156.4.

**Synthesis of 4a.** To a two-necked flask were added POCl$_3$ (1.76 g, 60%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 3.79 (s, 6 H), 6.84 ($d$, $J$ = 9 Hz, 4 H), 6.95 ($t$, $J$ = 6.9 Hz, 2 H), 7.04–7.11 (m, 12 H), 7.19–7.24 (m, 4 H), 7.40 ($d$, $J$ = 8.4 Hz, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 21.2, 122.2, 123.4, 124.1, 125.4, 127.3, 127.5, 130.2, 131.8, 133.4, 134.8, 136.5, 145.1, 146.8, 147.7. MS (FAB–MS) $m/z$: 569. Anal. Calcd for C$_{42}$H$_{36}$N$_2$: C, 88.69; H, 6.38; N, 4.93. Found: C, 88.4; H, 68.3; N, 4.95.9.

**Synthesis of 3b.** To a two-necked flask were added Cu (10.34 g, 83.4 mmol), K$_2$CO$_3$ (22.5 g, 162.8 mmol), 18-crown-6 ether (200 mg), N,N’-diphenylbenzidine (1) (5 g, 14.8 mmol), 4-iodotoluene (2b) (10.4 g, 44.4 mmol) and o-dichlorobenzene (100 mL). The reaction mixture was stirred and heated at 190 °C under N$_2$ for 24 h. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give a white solid, 3b (6.34 g, 83%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.32 (s, 6 H), 6.95–7.10 (m, 18 H), 7.20–7.24 (m, 4 H), 7.41 ($d$, $J$ = 8.4 Hz, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 21.1, 122.6, 123.8, 124.0, 125.3, 127.4, 129.4, 130.2, 133.1, 134.6, 145.7, 147.1, 148.1.
Synthesis of DVF-TFP. To a two-necked flask were added PPh3CH2Br (1.23 g, 3.4 mmol), NaH (0.079 g, 3.3 mmol) and dry THF (30 mL). The mixture was stirred at room temperature under N2 for 1 h, followed by adding 4b (1 g, 1.6 mmol) solution of dry THF (20 mL). The resulting reaction mixture was heated and stirred at 80 °C for 12 h. After cooling to room temperature, the solution was quenched by water and stirred for 5 min. The THF solvent was removed by rotary evaporator. The residue was extracted with ethyl acetate and water to remove the inorganic species. The organic layer was dried over MgSO4.

After removal of the solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give a white solid, DVF-TFP (0.38 g, 38%). 1H NMR (300 MHz, CDCl3): δ 5.17 (d, J = 10.8 Hz, 2 H), 5.65 (d, J = 17.4 Hz, 2 H), 6.67 (dd, J1 = 10.8 Hz, J2 = 17.4 Hz, 2 H), 7.00–7.05 (m, 16 H), 7.34–7.40 (m, 4 H), 7.53–7.56 (m, 4 H).

Synthesis of 3c. Pd3(dba)2 (0.6 g, 0.66 mmol) and tri-tert-butylphosphine (0.8 g, 4 mmol) were dissolved in dry toluene (20 mL) under N2 and the solution was stirred for 10 min at room temperature. The mixture was added to the toluene solution containing N,N'-diphenylbenzidine (1 g, 14.8 mmol), 4-fluoroiodobenzene (1 g, 14.8 mmol) and dry THF (20 mL). The mixture was stirred at room temperature under N2 for 12 h. After cooling to room temperature, the solution was quenched by water and stirred for 5 min. The THF solvent was removed by rotary evaporator. The residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give a white solid, 3c (0.6 g, 87%). 1H NMR (300 MHz, CDCl3): δ 7.06–7.25 (m, 18 H), 7.34–7.40 (m, 4 H), 7.53–7.56 (m, 4 H).

Synthesis of 3e. To a two-necked flask were added POCl3 (1.75 g, 11.4 mmol) and DMF (0.83 g, 11.4 mmol) by syringe at 0 °C, followed by adding 1,2-dichloroethane (50 mL) was then added, and the reaction mixture was stirred at room temperature under N2 for 30 min. 3e (0.5 g, 5.17 mmol) was then added, and the reaction mixture was heated at 80 °C under N2 for 6 h. After cooling to room temperature, the solution was quenched by NaOAc solution and stirred for 10 min. The resulting reaction mixture was heated and stirred at 80 °C for 30 min. 3c (0.5 g, 5.17 mmol) was then added, and the reaction mixture was stirred at room temperature under N2 for 12 h. After cooling to room temperature, the solution was quenched by water and stirred for 5 min. The THF solvent was removed by rotary evaporator. The residue was extracted with ethyl acetate and water to remove the inorganic species. The organic layer was dried over MgSO4.

After removal of the solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give a white solid, DVF-TFP (0.38 g, 38%). 1H NMR (300 MHz, CDCl3): δ 5.17 (d, J = 10.8 Hz, 2 H), 5.65 (d, J = 17.4 Hz, 2 H), 6.67 (dd, J1 = 10.8 Hz, J2 = 17.4 Hz, 2 H), 7.00–7.05 (m, 16 H), 7.34–7.40 (m, 4 H), 7.53–7.56 (m, 4 H).