# CHEMISTRY OF MATERIALS

## Bipolar Phenanthroimidazole Derivatives Containing Bulky Polyaromatic Hydrocarbons for Nondoped Blue Electroluminescence Devices with High Efficiency and Low Efficiency Roll-Off

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**Supporting Information** 

**ABSTRACT:** A series of bipolar phenanthroimidazole derivatives, TTP-TPI, DPT-TPI, and DPF-TPI, were designed and synthesized by incorporating polyaromatic hydrocarbon groups to phenanthroimidazole through a phenyl bridge. The bulky polyaromatic hydrocarbon units endow the molecules with high glass-transition temperatures, nonplanar twisty structures which reduce molecular aggregations. The bipolar transporting natures of these materials are demonstrated by single-carrier devices with supported of theoretical calculations. Nondoped organic light-emitting devices (OLEDs) using these phenanthroimidazole derivatives as emitters show blueviolet to sky-blue emissions with Commission Internationale de l'Eclairage (CIE) coordinates of (0.16, 0.05) for TTP-TPI, (0.16, 0.07) for DPT-TPI, and (0.17, 0.24) for DPF-TPI. The TTP-TPI-, DPT-TPI-, and DPF-TPI-based nondoped devices show impressive external quantum efficiencies (EQE) of 5.02, 5.25, 4.85%, respectively (corresponding current efficiencies: 2.10, 3.13, and 8.41 cd/A). These values are the best or among the best comparing to those of the reported nondoped OLEDs with the



corresponding color gamuts. These devices also show small efficiency roll-off at high brightness  $(1000 \text{ cd/m}^2)$  with EQEs drop by 20.7, 12, and 0%. Moreover, with well-balanced carrier transport, DPF-TPI based device can achieve a higher brightness of 10000 cd/m<sup>2</sup> with EQE maintaining at 4.49% (only drop by 7.4%).

**KEYWORDS:** organic light-emitting diodes, phenanthroimidazole, blue emitters, fluorescence

#### INTRODUCTION

Blue organic light-emitting materials have attracted much attention because of their significant applications in flat-panel displays and solid-state lighting.<sup>1</sup> Especially in full-color displays, the blue emitter can not only effectively reduce the power consumption of the devices but also be utilized to generate emission of other colors by energy transfer to a suitable emissive dopant.<sup>2</sup> However, high-performance blue emitters are still relatively rare.

To obtain high efficiency, phosphorescent organic lightemitting devices (PhOLEDs) have attracted intense interest as they can approach 100% internal quantum efficiency by utilizing both singlet and triplet excitons.<sup>3,4</sup> However, PhOLEDs typically have shorter lifetime and sharper efficiency roll-off at high brightness. In addition, it is difficult to synthesize efficient deepblue phosphors, because of the additional nonradiative pathway via the metal d-orbitals when regulating the emissive metal– ligand charge-transfer (MLCT) band into the deep blue.<sup>5</sup> Therefore, fluorescent emitters are used for most high-efficiency blue and deep-blue OLEDs.

Charge transport and balance are two crucial factors for obtaining high efficiency and stable OLEDs.<sup>6</sup> One promising strategy for this demand is to simultaneously incorporate electron-donor and electron-acceptor groups into a single molecule to obtain materials with bipolar transporting properties. This could facilitate better balanced transports of both holes and electrons, and broaden the exciton formation zone, consequently improving the device performance and reducing efficiency roll-off.<sup>7</sup> However, for application in blue OLEDs, this strategy does have some disadvantages, such as a huge bathochromic effect,<sup>8</sup> low quantum yield due to the dipolar quenching,<sup>9</sup> as well as the unavoidable decrease in band gap of the material due to intramolecular charge transfer.<sup>10</sup> To address

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these issues, one possible approach is to interrupt the  $\pi$ conjugation between the donor and the acceptor groups with a Si or other sp<sup>3</sup>-hybridized atom. For example, Ma and Yang developed a series of silicon-bridged host materials containing both arylamine and heterocyclic groups for efficient PhOLEDs.<sup>7a,11</sup> However, this kind of material still cannot serve as an efficient emitter for nondoped OLEDs because their emission peaks would typically blue-shifted to the ultraviolet region. On the other hand, Adachi et al. recently reported a series of materials with thermally activated delayed fluorescence (TADF).<sup>12</sup> In these materials, reverse intersystem crossing (RISC) from triplet to singlet states can be thermally activated and thus enable a potentially 100% internal singlet yields. As highly efficient TADF materials also need to be doped in appropriate host materials to avoid concentration quenching of the triplet excitons. Hence, high-performance bipolar hosts with sufficiently wide energy gap are also desirable.

Phenanthroimidazole is a near-ultraviolet emitter with dual nature due to different bonding structures of two nitrogen atoms at the imidazole ring. It exhibits electron-donating properties when a neutral or an electron-withdrawing moiety is attached to its 2-position,<sup>13</sup> but it shows electron withdrawing properties when linked with an electron donor.<sup>14</sup> Polycyclic aromatic hydrocarbon units (Müllen dendrons) have been shown to be effective molecular building blocks for inhibiting molecular aggregation or  $\pi$ - $\pi$  stacking in the solid state.<sup>15</sup> In addition, the polyphenylated aromatic cores could serve as a platform for tuning of donor–acceptor interactions.<sup>16</sup> It can also act as a  $\pi$ -acceptor and be incorporated to an electron donor to form bipolar molecule.<sup>17</sup>

Herein, we designed and synthesized a series of new materials, TTP-TPI, DPT-TPI and DPF-TPI, by combining phenanthroimidazole and bulky polyaromatic hydrocarbon groups. It is anticipated that the electron-donating and -accepting groups would impart the material with bipolar transporting nature; meanwhile, emission spectra of the molecule are expected to redshift to the blue region due to the increase in conjugation length. We also expect that the materials to possess good thermal and morphological stability as a result of the bulky polyaromatic hydrocarbon groups. Thermal, photophysical, and electroluminescent properties of the compounds were comprehensively investigated. The new phenanthroimidazole derivatives have been demonstrated as excellent blue fluorescent emitters for nondoped OLEDs.

#### EXPERIMENTAL SECTION

Starting materials 4-ethynylbenzaldehyde,<sup>18</sup> 1,3-diphenyl-2*H*-cyclopenta[1] phenanthren-2-one,<sup>19</sup> and 7,9-diphenyl-8*H*-cyclopenta-[a]acenaphthylen-8-one<sup>20</sup> were synthesized according to the literature procedures. All other chemicals and solvents were used as received from commercial suppliers without further purification.

**Syntheses.** 1-(4-(Tert-butyl)phenyl)-2-(4-ethynylphenyl)-1*H*-phenanthro[9,10-*d*]imidazole (1). The product was prepared by refluxing 9,10-phenanthrenequinone (2.08 g, 10.0 mmol), 4-ethynyl-benzaldehyde (1.30 g, 10.0 mmol), 4-tert-butylbenzenamine (1.97 g, 12.0 mmol), and ammonium acetate (7.71 g, 100 mmol) in glacial acetic acid (60 mL) for 24 h under an argon atmosphere. After cooling to room temperature, a pale yellow mixture was obtained and poured into a methanol solution with stirring. The separated solid was filtered off, washed with methanol, and dried to give a pale yellow solid. The solid was purified by column chromatography (petroleum ether:CH<sub>2</sub>Cl<sub>2</sub> = 3:1) on silica gel. A yellow powder was finally obtained after it was stirred in refluxing ethanol, subsequently filtered and dried in vacuum. Yield: 3.71 g (82.3%). <sup>1</sup> H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.77 (ddd, *J* = 25.0, 12.8, 4.7 Hz, 3H), 7.77–7.73 (m, 1H), 7.69–7.63 (m, 3H), 7.58–7.51

(m, 3H), 7.46–7.40 (m, 4H), 7.26 (ddd, J = 18.2, 8.3, 7.2 Hz, 2H), 3.21 (s, 1H), 1.45 (s, 9H). MS (ESI<sup>+</sup>): m/z 450.14 (MH<sup>+</sup>). Calcd for C<sub>33</sub>H<sub>26</sub>N<sub>2</sub>: 450.57.

1-(4-(Tert-butyl)phenyl)-2-(3',4',5'-triphenyl-[1,1':2',1"-terphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazole (TTP-TPI). Compound 1 (1.23 g, 2.73 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (0.95 g, 2.48 mmol) were dissolved in *o*-xylene (70 mL) under an argon atmosphere, and the resultant mixture was heated for 24 h at 150 °C. After the mixture was cooled to room temperature, ethanol (100 mL) was added. The precipitate was filtered, washed with ethanol (100 mL), and dried in a vacuum. Following column chromatography (petroleum ether:CH<sub>2</sub>Cl<sub>2</sub> = 1:1) on silica gel, TTP-TPI was obtained as a white powder. Yield: 1.70 g (85.0%). <sup>1</sup> H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.66 (dd, J = 20.7, 8.4 Hz, 3H), 7.66 (t, J = 7.3 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.55-7.51 (m, 2H), 7.43 (s, 2H), 7.34 - 7.30 (m, 4H), 7.19 (s, 1H), 7.11–7.07 (m, 6H), 7.02 (d, J = 8.4 Hz, 2H), 6.90 – 6.84 (m, 6H), 6.82 - 6.77 (m, 7H), 6.74 (dd, J = 6.6, 3.2 Hz, 2H), 1.36 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.35, 146.16, 141.85, 141.56, 140.82, 140.14, 139.83, 139.62, 139.16, 131.50, 131.41, 131.27, 129.90, 129.76, 128.65, 128.42, 127.60, 127.25, 126.97, 126.91, 126.62, 126.30, 125.73, 125.63, 125.34, 124.04, 123.05, 120.91, 35.00, 31.41 ppm. MS (ESI<sup>+</sup>): m/z 807.51 (MH<sup>+</sup>). Calcd for C<sub>61</sub>H<sub>46</sub>N<sub>2</sub>: 807.03.

1-(4-(Tert-butyl)phenyl)-2-(4-(1,4-diphenyltriphenylen-2-yl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole (DPT-TPI). Using a similar synthesis procedure for TTP-TPI by a Diels—Alder reaction, beige powder was finally obtained. Yield: 1.32 g (80.2%). <sup>1</sup> H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.79 (dd, *J* = 20.5, 8.3 Hz, 3H), 8.49 (d, *J* = 8.2 Hz, 2H), 7.79 (s, 1H), 7.74 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.72–7.64 (m, 4H), 7.57–7.51 (m, 4H), 7.50–7.43 (m, 9H), 7.33 – 7.22 (m, 5H), 7.16–7.11 (m, 3H), 7.08–7.02 (m, 3H), 1.49 (s, 9H). <sup>13</sup> C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.26, 141.73, 139.31, 138.14, 137.90, 137.25, 136.49, 132.17, 132.06, 131.91, 131.62, 131.38, 130.62, 130.06, 129.75, 129.63, 129.11, 128.71, 128.47, 127.25, 126.98, 126.78, 126.45, 126.24, 125.57, 125.27, 124.05, 123.21, 123.07, 120.92, 119.53, 112.75, 35.01, 31.42 ppm. MS (ESI<sup>+</sup>): *m/z* 805.14 (MH<sup>+</sup>). Calcd for C<sub>61</sub>H<sub>44</sub>N<sub>2</sub>: 805.02.

1-(4-(Tert-butyl)phenyl)-2-(4-(7,10-diphenylfluoranthen-8-yl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole (DPF-TPI). Using a similar synthesis procedure for TTP-TPI by a Diels–Alder reaction, yellowgreen powder was finally obtained. Yield: 1.57 g (84.9%). <sup>1</sup> H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.76 (dd, *J* = 20.6, 8.4 Hz, 3H), 7.78 (t, *J* = 8.2 Hz, 3H), 7.73 – 7.66 (m, 3H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.45 (dt, *J* = 4.5, 2.5 Hz, 6H), 7.42 (d, *J* = 2.8 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.20 (dd, *J* = 8.4, 2.2 Hz, 3H), 6.70 (d, *J* = 7.0 Hz, 1H), 1.47 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.86, 138.98, 138.29, 137.94, 136.46, 136.06, 135.76, 133.08, 131.00, 130.28, 129.79, 129.67, 129.08, 128.66, 128.53, 128.40, 127.87, 127.63, 127.44, 126.99, 126.74, 126.25, 124.04, 123.40, 123.04, 120.92, 35.02, 31.41 ppm. MS (ESI<sup>+</sup>): *m*/z 779.04 (MH<sup>+</sup>). Calcd for C<sub>59</sub>H<sub>42</sub>N<sub>2</sub>: 778.98.

Characterization. Nuclear magnetic resonance (<sup>1</sup> NMR) spectra were recorded using  $CD_2Cl_2$  (<sup>1</sup> H NMR) and  $CDCl_3$  (<sup>13</sup> C NMR) as solvent with a Varian Gemin-400 Varian spectrometer. Mass spectra were recorded on a PE SCIEX API-MS system. Absorption and photoluminescence (PL) spectra of the materials were recorded with a PerkinElmer Lambda 2S UV/vis spectrophotometer and a Perkin-Elmer LS50B luminescence spectrophotometer, respectively. Thermogravimetric analysis (TGA) measurements were performed on a TA Instrument TGAQ50 at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetric (DSC) measurements were performed on a TA Instrument DSC2910. The samples were first heated at a rate of 10 °C/min to melt and then quenched. Glass transition temperature  $(T_{o})$  and crystallization temperature  $(T_{c})$  were recorded by heating the quenched samples at a heating rate of 10 °C/ min. The HOMO energy of the materials were measured directly by ultraviolet photoelectron spectroscopy (UPS), whereas the LUMO energy was estimated by subtracting the HOMO energy with the optical band gap determined from the lowest energy absorption edge of the absorption spectrum.

**Device Fabrication and Measurement.** Patterned indium tin oxide (ITO) glass with a sheet resistance of 15  $\Omega$  per square was used as



the substrate. Before device fabrication, the ITO glass substrates were cleaned with isopropanol, Decon 90 and deionized water, dried in an oven at 120 °C, treated with UV-ozone, and finally transferred to a vacuum deposition system with a base pressure better than  $5 \times 10^{-4}$  Pa for organic and metal deposition. Devices were fabricated by thermal deposition of organic layers at a deposition rate of 1-2 Å/s. The cathode was completed through thermal deposition of LiF at a deposition rate of 0.1 Å/s, followed by Al deposition at a rate of 10 Å/s. Electroluminescence (EL) spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current–voltage–luminance characteristics were measured with a computer-controlled Keitheley 2400 sourcemeter under ambient atmosphere.

#### RESULTS AND DISCUSSION

Synthesis and Characterization. Synthetic routes and chemical structures of the compounds. 1-(4-(tert-butyl)phenyl)-2-(3',4',5'-triphenyl-[1,1':2',1"-terphenyl]-4-yl)-1Hphenanthro[9,10-d]imidazole (TTP-TPI), 1-(4-(tert-butyl)phenyl)-2-(4-(1,4-diphenyltriphenylen-2-yl)phenyl)-1Hphenanthro[9,10-d]imidazole (DPT-TPI) and 1-(4-(tert-butyl)ph-enyl)-2-(4-(7,10-diphenylfluoranthen-8-yl)phenyl)-1Hphenanthro[9,10-d]imidazole (DPF-TPI) are depicted in Scheme 1. A key intermediate 1-(4-(tert-butyl)phenyl)-2-(4ethynylphenyl)-1H-phenanthro[9,10-d]imidazole (1) was prepared according to the literature.<sup>21</sup> The Diels-Alder reaction between compound 1 and 2,3,4,5-tetraph-enylcyclopenta-2,4dienone, 1,3-diphenyl-2H-cyclopenta[l]phenanthren-2-one or 7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one give rise to the final products TTP-TPI, DPT-TPI, and DPF-TPI, respectively. All the compounds were purified with the silica column method. Chemical structures of all of the compounds were fully characterized with <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and mass spectrometry. Detailed synthetic procedures and characterization of the new compounds have been described in the Experimental Section.

Thermal Properties. Thermal properties of the three phenanthroimidazole derivatives were investigated by thermog-



Figure 1. DSC curves for (a) DPT-TPI and (b) DPF-TPI.

ravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. All the compounds exhibited good thermal stability. As shown in Figure S1 in the Supporting Information, decomposition temperatures ( $T_{dy}$ )



### Table 1. Key Physical Properties of the Three Compounds

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Figure 2. UV-vis absorption (left panel) and PL spectra (right panel) of TTP-TPI, DPT-TPI, and DPF-TPI in THF solution (solid symbols) and in thin film (open symbols).

Wavelength (nm)



Figure 3. Optimized molecular geometries and the calculated spatial distributions of the HOMOs and the LUMOs of TTP-TPI, DPT-TPI, and DPF-TPI.

defined as temperature at which there is a 5% weight loss), were measured to be 421, 458, and 439 °C for TTP-TPI, DPT-TPI, and DPF-TPI, respectively. DSC measurements were performed, from 20 to 355 °C for all of the materials. During the first heating process, DPF-TPI only shows an endotherimic peak at a melting point  $(T_m)$  of 351 °C. When the sample was heated again, a glasstransition revealed at 176 °C. Thermal properties of DPT-TPI are similar to those of DPF-TPI except for an additional phase

transformation at 316 °C ( $T_1$ ), and exhibited a  $T_g$  and a  $T_m$  of 197 and 335 °C, respectively. No obvious glass transition and endothermic melting transition were observed for TTP-TPI and it is most likely due to its smaller heat capacity and crystallinity. Figure 1 shows the DSC curves of DPT-TPI and DPF-TPI. Key thermal data of the phenanthroimidazole derivatives are summarized in Table 1. As expected, the new materials have much better thermal properties than their parent molecule 1,2-

Table 2. EL Performance of the Phenanthroimidazole Derivatives

			maximum						
emitter	$\begin{pmatrix} V_{\mathrm{on}}^a \\ \mathrm{(V)} \end{pmatrix}$	${\eta_{\rm C}}^b({\rm cd/A})$	$\eta_{\rm P}{}^b({\rm lm/W})$	$\eta_{\text{ext}}^{\ \ b}(\%)$	$\eta_{\rm C}{}^{b}({\rm cd/A})$	${\eta_{\mathrm{P}}}^{b}(\mathrm{lm/W})$	$\eta_{\rm ext}^{\ \ b}(\%)$	$\lambda_{\rm EL}^{c}$ (nm)	CIE $(x, y)$
TTP-TPI	3.1	$2.10 \\ (2.06 \pm 0.04)$	$     \begin{array}{r}       1.88 \\       (1.85 \pm 0.03)     \end{array} $	5.02 (4.94 ± 0.08)	1.47 (1.44 ± 0.03)	0.81 (0.79 ± 0.02)	3.98 (3.90 ± 0.08)	424	0.16, 0.05
DPT-TPI	2.9	3.13 (3.09 ± 0.05)	3.22 (2.96 ± 0.26)	5.25 (5.19 $\pm$ 0.07)	$2.78 \\ (2.75 \pm 0.03)$	$\begin{array}{c} 1.92 \\ (1.84 \pm 0.08) \end{array}$	$\begin{array}{c} 4.62 \\ (4.55 \pm 0.07) \end{array}$	432	0.16, 0.07
DPF-TPI	2.7	8.41 (8.33 ± 0.11)	$7.23 \\ (6.91 \pm 0.32)$	$\begin{array}{c} 4.85 \\ (4.83 \pm 0.04) \end{array}$	$8.40 \\ (8.32 \pm 0.08)$	5.69 (5.55 ± 0.14)	$\begin{array}{c} 4.85 \\ (4.82 \pm 0.03) \end{array}$	468	0.17, 0.24

 ${}^{a}V_{on}$  is the turn-on voltage at 1 cd/m<sup>2</sup>.  ${}^{b}\eta_{C}$ ,  $\eta_{P}$ , and  $\eta_{ext}$  are the current, power, and external quantum efficiency, respectively. Order of measured efficiency values: maximum and average values in parentheses, averaged from four devices.  ${}^{c}$ The maximum electroluminescence wavelength.



**Figure 4.** EL spectra of the (a) TTP-TPI-, (b) DPT-TPI-, and (c) DPF-TPI-based devices viewed in the normal direction at a luminance of 10, 100, and 1000  $cd/m^2$ .

diphenyl-1*H*-phenanthro[9,10-*d*]imidazole (PPI,  $T_g = 62 \degree C$ ,  $T_d = 340 \degree C$ ).<sup>22</sup> The results confirm that introduction of highly twisted and bulky polyaromatic hydrocarbons can greatly



**Figure 5.** Current density–voltage–luminance (J-V-L) characteristics of the OLEDs based on the three phenanthroimidazole derivatives.



Figure 6. Energy level diagrams of the three phenanthroimidazolederivative-based devices.

improved their morphological stability, which is highly important for applications in organic electronic devices.

**Optical Properties.** Figure 2 shows normalized UV–vis absorption and PL spectra of TTP-TPI, DPT-TPI, and DPF-TPI in diluted THF solutions and as thin film prepared by thermal evaporation on quartz plates. Key photophysical data of the three compounds are summarized in Table 1. These materials show two similar absorption peaks in solution while showing slight bathochromic shifts in the film state. A higher intensity absorption band around 260 nm are probably originated from the  $\pi$ - $\pi$ \* transition of their common benzene ring, and a lower intensity band around 330–370 nm can be assigned to the delocalized  $\pi$ - $\pi$ \* transition of the phenanthroimidazole.<sup>23</sup> In addition, DPT-TPI and DPF-TPI exhibit appreciable absorption band in the range of 284–304 nm, which can be attributed to the  $\pi$ - $\pi$ \* transition in the aryl core of the polyaromatic hydrocarbon groups.<sup>24</sup> As shown in Figure 2, all of the three compounds



**Figure 7.** Current efficiency and power efficiency versus current density curves of the (a) TTP-TPI-, (b) DPT-TPI-, and (c) DPF-TPI-based devices. (d) EQE of the three devices at different luminances.

exhibit blue emissions with an emission peak ranging from 406 to 472 nm. Compared to the PL spectra of TTP-TPI, the PL spectra of DPT-TPI and DPF-TPI show further bathochromic shift which could be attributed to the increase in  $\pi$  conjugation of the

end-capping polyaromatic hydrocarbon groups. It should be noted that all compounds show only small peak shifts in their absorption and PL spectra from THF solutions to solid states. This indicates that the highly twisted substituent on the 1imidazole position as well as the noncoplanar polyaromatic hydrocarbon moieties can effectively suppress intermolecular aggregation in the solid state. In addition, fluorescent quantum vields of TTP-TPI, DPT-TPI and DPF-TPI were estimated to be approaching unity in dichloromethane using 9,10-diphenylanthracene as a standard ( $\Phi_f = 0.90$  in cyclohexane).<sup>25</sup> The optical band gaps  $(E_{\alpha})$  determined from the threshold of the optical absorption are 3.26, 3.21, and 2.99 eV for TTP-TPI, DPT-TPI and DPF-TPI, respectively. The highest occupied molecular orbital (HOMO) levels as measured by using ultraviolet photoelectron spectroscopy (UPS) were -5.67, -5.68, and -5.58 eV, respectively. The lowest unoccupied molecular orbital (LUMO) levels of these compounds are estimated to be -2.41, -2.47, and -2.59 eV respectively by adding the corresponding  $E_{\rm g}$ to the HOMO values.

Theoretical Properties. To better understand the structure-property relationship of the three phenanthroimidazole derivatives at molecular level, we carried out density functional theory (DFT) calculations with the geometry optimized at the B3LYP/6-31G (d) theoretical level. The optimized geometry and electron density distribution of the frontier molecular orbitals are shown in Figure 3. All three molecules have highly twisted conformation because of the large torsional angle between t-Bu-benzene and phenanthroimidazole moieties, and the steric hindrance of end-capping polyaromatic hydrocarbon groups. Such highly twisted conformation can effectively reduce intermolecular interaction and suppress problematic recrystallization, consequently leading to low fluorescence quenching and stable amorphous thin films. According to DFT calculations, the shapes of the HOMO orbitals are very similar, mainly located on the phenanthroimidazole moiety and the phenyl group at the 2position of imidazole. However, their LUMO shapes are different, and with increased conjugation length of Müllen dendron groups from TTP-TPI to DPF-TPI, the LUMO orbitals are gradually localized on polyaromatic hydrocarbon groups. It can be seen that all of the materials show clear separation of HOMO and LUMO at the hole and the electron transporting moieties respectively, especially for DPF-TPT, the HOMO and LUMO orbitals are completely separated.

Electroluminescence Properties. To evaluate the bipolar charge transporting properties of the compounds, we fabricated single-carrier devices with structures of indium tin oxide (ITO)/ N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl- 4,4'-diamine (NPB, 20 nm)/TTP-TPI or DPT-TPI or DPF-TPI (80 nm)/NPB (20 nm)/Al (150 nm) for hole-only devices and ITO/ 1,3,5-tri(phenyl-2-benzimidazolyl)-benzene (TPBI, 20 nm)/ TTP-TPI or DPT-TPI or DPF-TPI (80 nm)/TPBI (20 nm)/ LiF (1 nm)/Al (150 nm) for electron-only devices. NPB and TPBI were used to prevent electron and hole injection from the cathode and anode, respectively.<sup>26</sup> As shown in Figure S2 in the Supporting Information, the current density-voltage (J-V)characteristics of the single-carrier devices illustrate that the three phenanthroimidazole derivatives are capable of transporting both holes and electrons. Among them, TTP-TPI based devices exhibited a lower charge transporting properties, which may be attributed to the conjugation of a relatively small polyaromatic hydrocarbon group due to the large torsional angle between the dendron core and all peripheral phenyl groups. In addition, because the HOMO and LUMO orbitals are completely

Table 3. Key Performance Parameters of the TTP-TPI-, DPT-TPI-, and DPF-TPI-Based Devices and Other High Performance Blue-Violet, Deep-Blue, and Sky-Blue Light-Emitting Devices with  $CIE_y < 0.06$ ,  $0.06 < CIE_y < 0.10$ , and  $0.15 < CIE_y < 0.25$ , Respectively

color	emitter	$V_{\mathrm{on}}{}^{a}(\mathrm{V})$	$\lambda_{\rm EL}{}^{c}$ (nm)	${\eta_{\mathrm{C}}}^d(\mathrm{cd}/\mathrm{A})$	${\eta_{\mathrm{P}}}^d(\mathrm{lm/W})$	$\eta_{\mathrm{ext}}^{d}$ (%)	CIE $(x, y)$	ref
blue-violet	TTP-TPI	3.1	424	2.10/1.47 <sup>e</sup>	1.88/0.81 <sup>e</sup>	5.02/3.98 <sup>e</sup>	0.16, 0.05	this work
	BPA-BPI	2.0	428	0.65/-	0.68/-	1.37/-	0.15, 0.05	14a
	PATPA	3.8	424	0.34/-	0.24/-	0.72/-	0.15, 0.06	14a
	TDAF1	4.0 <sup>b</sup>		1.53/-		5.30/-	0.158, 0.041	35
	TDAF2	4.0 <sup>b</sup>		1.10/-		4.10/-	0.160, 0.044	35
	CPhBzIm	4.0 <sup>b</sup>	426	1.60/-	1.07/-	$3.0/2.4^{e}$	0.16, 0.05	36
	TPA-(3)-F		428	0.39/-			0.16, 0.06	37
	M1		420	0.65/-	0.48/-	1.94/-	0.165, 0.050	38
	M2		428	1.53/-	0.86/-	3.02/-	0.166, 0.056	38
	TPAXAN	3.4	428			4.62/3.0 <sup>b,e</sup>	0.155, 0.049	39
deep-blue	DPT-TPI	2.9	432	3.13/2.78 <sup>e</sup>	$3.22/1.92^{e}$	5.25/4.62 <sup>e</sup>	0.16, 0.07	This work
	PhQ-CVz	$3.5^{b}$		2.06/-	1.77/0.51 <sup>b,e</sup>	$2.45/2.0^{b,e}$	0.156, 0.093	2c
	CzPhB	6.5	449	$3.3/2.6^{b,e}$	1.3/-	$4.3/3.9^{b,e}$	0.15, 0.09	8
	TPA-BPI	2.8	448	2.63/2.42 <sup>e</sup>	2.53/0.97 <sup>e</sup>	3.08/2.88 <sup>e</sup>	0.15, 0.09	14a
	TPIP	3.9	445	4.69/-	$2.71/1.6^{b}$	5.43/-	0.15, 0.09	21
	$Be(PPI)_2$	3.2		2.41/2.04 <sup>e</sup>	2.52/0.95 <sup>e</sup>	2.82/2.40 <sup>e</sup>	0.15, 0.09	26b
	$Zn(PPI)_2$	3.2		$2.06/0.74^{e}$	$2.02/0.26^{e}$	2.08/0.75 <sup>e</sup>	0.15, 0.09	26b
	POAn	3.0	445	$3.2/2.3^{b,e}$	3.3/-	$4.7/3.3^{b,e}$	0.15, 0.07	40
	9TPAFSPO	3.3		$1.50/0.50^{b,e}$	$2.19/0.20^{b,e}$	$2.71/0.80^{b,e}$	0.16, 0.07	41
	9DPNAFSPO	3.1	424	$1.18/0.80^{b,e}$	$1.13/0.25^{b,e}$	1.96/1.10 <sup>b,e</sup>	0.15, 0.07	41
	NAF1	3.8	448	3.56/3.10 <sup>b,e</sup>	$2.10/1.60^{b,e}$	4.02/-	0.15, 0.09	42
	TBMFA	3.2	444	1.79/-	1.41/-	$3.58/2.10^{b,e}$	0.151, 0.085	43
	TBDNPA	3.0	444	2.63/-	1.96/-	5.17/4.10 <sup>b,e</sup>	0.149, 0.086	43
	TBMFPA	3.2	448	2.67/-	1.92/-	4.76/4.0 <sup>b,e</sup>	0.147, 0.096	43
	TFSDTC	$7.5^{b}$	432	$1.91/1.70^{b,e}$		2.7/-	0.15, 0.07	44
	1	3.5	428	$2.2/1.1^{b,e}$	1.6/-	2.9/-	0.17, 0.07	45
	BPPI	4.0	444	1.25/-	,	3.16/2.75 <sup>b,e</sup>	0.15, 0.07	46
sky-blue	DPF-TPI	2.7	468	$8.41/8.40^{e}/7.69^{f}$	$7.23/5.69^{e}/3.23^{f}$	4.85/4.85 <sup>e</sup> / 4.49 <sup>f</sup>	0.17, 0.24	this work
	B3	2.7	468	3.63/3.40 <sup>b</sup>	2.60/-	2.41/-	0.14, 0.21	7b
	BPPI	3.8		6.62/6.56 <sup>e</sup>	4.10/3.2 <sup>e</sup>	$3.60/3.4^{e}$	0.16, 0.23	22
	B2PPQ	3.0	459	$7.12/7.12^{b,e}/5.5^{b,f}$	$6.56/6.55^{b}/1.40^{bf}$	4.30/-/-	0.15, 0.16	28
	Ph3TPE	3.7	467	3.70/1.50 <sup>b,e</sup>	$2.50/0.5^{b,e}$		0.17, 0.20	29
	DFDF	3.7	474	3.80/3.55 <sup>b,e</sup>	2.60/-	$2.30/2.10^{b,e}$	0.16, 0.23	30
	1-NaCPI	2.73	468	$4.36/4.35^{b,e}$	$3.22/2.20^{b,e}$	2.88/-	0.166, 0.20	31
	2-NaCPI	2.71	460	$4.65/4.62^{b,e}$	3.18/2.20 <sup>b,e</sup>	3.61/-	0.151, 0.161	31
	PhSPDPV		478	5.4/-	$5.7/3.0^{b,e}$	$3.4/3.0^{b,e}$	0.14, 0.22	32
	PhAA	3.2	470	$4.0/3.6^{b,e}$	4.0/-		0.14, 0.20	33
	NAA	2.9	472	$5.5/5.3^{b,e}$	3.5/-		0.14, 0.21	33
	Py-TPI	3.4	468	$3.93/3.90^{b,e}$	$3.2/1.5^{b,e}$		0.16, 0.20	34

 ${}^{a}V_{on}$  is turn-on voltage at 1 cd/m<sup>2</sup>.  ${}^{b}V$ alues are estimates from the original figures.  ${}^{c}T$ he maximum electroluminescence wavelength.  ${}^{d}\eta_{c}$ ,  $\eta_{p}$ , and  $\eta_{ext}$  are current, power, and external quantum efficiencies, respectively. Efficiency values without superscript are maximum values; superscripts  ${}^{e}$ Efficiencies measured at 1000 cd/m<sup>2</sup>.  ${}^{f}$ Efficiencies measured at 1000 cd/m<sup>2</sup>.

separated, DPF-TPI possess a more balanced charge transport ability than TTP-TPI and DPT-TPI, which could support the following explanation on the lower efficiency roll-off of the DPF-TPI based device.

To investigate electroluminescence (EL) properties of the three phenanthroimidazole derivatives, we fabricated nondoped devices with a configuration of ITO/NPB (70 nm)/4,4',4"-tri(N-carbazolyl)-triphenylamine (TCTA, 5 nm)/TTP-TPI or DPT-TPI or DPT-TPI or DPF-TPI (30 nm)/TPBI (30 nm)/LiF (1 nm)/Al (150 nm). In these devices, ITO and LiF/Al were used as the anode and the cathode, respectively; NPB was used as the hole-transporting layer (HTL); TCTA was used as a buffer layer;<sup>14b</sup> TPBI was used as the electron-transporting layer (ETL) and hole-blocking layer; and the three newly synthesized phenanthroimidazole derivatives were used as the emitting layer (EML).

Key device performance parameters are summarized in Table 2 (Detailed parameters of replicate devices are summarized in the Supporting Information, Figure S3 and Table S1).

Figure 4 depicts EL spectra of the three devices viewed in the normal direction at a luminance of 10, 100, and 1000 cd/m<sup>2</sup>. Peak wavelengths of the EL spectra for the devices using TTP-TPI, DPT-TPI and DPF-TPI as the EML are 424, 432, and 468 nm, respectively. The EL spectra of the devices are almost the same as the corresponding PL spectra in the film state, except for small blue-shifts of DPT-TPI and DPF-TPI. This suggests that the EL is indeed from the three phenanthroimidazole derivatives. In addition, no excimer or exciplex emission can be observed. It is attributed to the highly twisted structure due to the substituent on the 1-imidazole position and the noncoplanar polyaromatic hydrocarbon moieties, which results in large steric hindrance

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toward the phenanthroimidazole unit and the end group. As a result, it prevents close-packing of the molecules. It is worth noting that the EL spectra for the three devices are almost independent of the driving voltages, with the spectrum remained unchanged over a wide luminance range of  $10-1000 \text{ cd/m}^2$ . It suggests that the hole and electron recombination is well confined within the EML, which might result from the wide band gaps of the adjacent TCTA (3.4 eV) and TPBI (3.5 eV) layers. The emission color ranged between blue-violet to sky-blue with CIE 1931 chromaticity coordinates of (0.16, 0.05), (0.16, 0.07), and (0.17, 0.24) for the devices based on TTP-TPI, DPT-TPI, and DPF-TPI, respectively. In particular, the CIE coordinates of the DPT-TPI-based device are close to the blue standards (0.14, 0.08) of the National Television Standards Committee (NTSC).<sup>27</sup>

Current density—voltage—luminance (J-V-L) characteristics of the three devices are shown in Figure 5. All devices show low turn on voltage  $(V_{on})$  defined as voltage required to give a luminance of 1 cd/m<sup>2</sup>) from 2.7 to 3.1 V, which can be attributed to the small injection barriers in the devices. A schematic energy level diagram of these OLEDs is illustrated in Figure 6. All three compounds have similar HOMO at 5.7 eV, it mean that there are negligible hole-injection barriers at the TCTA/EML junction. The electron injection barriers at the TPBI/EML junction are 0.2 to 0.4 eV, and the hole injection barrier is also only 0.3 eV at the NPB/TCTA junction. These small injection barriers enable efficient injection of both holes and electrons into the emission layer.

Figure 7 shows the efficiency of the three devices. Among them, the DPF-TPI based sky blue device exhibits the best performance, with a maximum current efficiency ( $\eta_{C, max}$ ) of 8.41 cd/A, a maximum power efficiency ( $\eta_{\rm P, max}$ ) of 7.23 lm/W, and a maximum external quantum efficiency ( $\eta_{\text{ext, max}}$ ) of 4.85%. It is worth noting that the efficiency of DPF-TPI-based device remains at 4.85% (8.40 cd/A) at a brightness of 1000 cd/m<sup>2</sup>. Even at a much higher brightness of 10000  $cd/m^2$ , the external quantum efficiency is still 4.49% with a small roll-off of 7.42% (Figure 7d). To the best of our knowledge, this is the best result reported in sky-blue nondoped OLEDs (Table 3).7b,22,28-34 The low efficiency roll-off at high luminance for DPF-TPI-based device can be attributed to the use of the bipolar emitter, which may result in balanced charge fluxes and a broad distribution of recombination regions within the emitting layer. Satisfactory EL efficiencies are also obtained from blue-violet and deep blue devices based on TTP-TPI and DPT-TPI, with  $\eta_{C, \text{ max}}$   $\eta_{P, \text{ max}}$ and  $\eta_{\rm ext,\ max}$  of 2.10 cd/A, 1.88 lm/W, and 5.02%; and 3.13 cd/A, 3.22 lm/W, and 5.25%, respectively. Though these two devices exhibited a slightly higher efficiency roll-off than the DPF-TPIbased device, the efficiencies are still as high as 3.98% (1.47 cd/ A) for the TTP-TPI device and 4.62% (2.78 cd/A) for the DPT-TPI device at a brightness of 1000 cd/m<sup>2</sup>. These performances are also among the best for either blue-violet<sup>14a,35–39</sup> or deep-blue<sup>2c,8,14a,21,26b,40–46</sup> nondoped OLEDs (Table 3).

#### CONCLUSION

In summary, we have designed and synthesized three novel bipolar phenanthroimidazole derivatives, TTP-TPI, DPT-TPI and DPF-TPI, containing different polyaromatic hydrocarbon moieties as the electron-transporting groups. These compounds show strong blue PL emissions and good thermal stability ( $T_d > 420$  °C). Theoretical calculations and single-carrier devices confirmed the bipolar transporting nature of these materials. We have also fabricated highly efficient blue-violet, deep-blue, and

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sky-blue nondoped OLEDs by using the phenanthroimidazole derivatives as fluorescent emitters. The TTP-TPI, DPT-TPI, and DPF-TPI-based nondoped devices can achieve excellent EQE (current efficiency) of 5.02% (2.10 cd/A), 5.25% (3.13 cd/A), and 4.85% (8.41 cd/A) with CIE coordinates of (0.16, 0.05), (0.16, 0.07) and (0.17, 0.24), respectively. These values are the best or among the best comparing to those of the reported nondoped OLEDs with the corresponding color gamuts. The DPF-TPI-based device exhibited lower efficiency roll-off than TTP-TPI and DPT-TPI-based devices, which could be attributed to its more balanced carrier transporting characteristic of DPF-TPI. Our study presents a new molecular design strategy of bipolar fluorescent emitters for efficient nondoped OLEDs.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

TGA curves, *J*–*V* characteristics for single-carrier devices, and EL performance of replicate devices are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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