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Carbazolylphosphines and Carbazolylphosphine Oxides: Facilely Synthesized Host Materials with Tunable Mobilities and High Triplet Energy Levels for Blue Phosphorescent Organic Light-Emitting Diodes

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ABSTRACT: High triplet energy level (E_T) and balanced carrier mobility are critical factors for host materials in efficient blue phosphorescent organic light-emitting diodes (PHOLEDs). Herein, we report the facile synthesis of four compounds, dicarbazolylphenylphosphine (DCPP), dicarbazolylphenylphosphine oxide (DCPPO), tricarbazolylphosphine (TCP), and tricarbazolylphosphine oxide (TCPO), and their application as host materials for a classic blue phosphorescent emitter bis[2-(4,6difluorophenyl)pyridinato- C^2 ,N](picolinato)iridium(III) (FIrpic). The four compounds show high E_T up to 3.0 eV and tunable mobilities. We fabricated four OLEDs with a device structure of ITO/MoO₃ (1 nm)/N,N'-dicarbazolyl-3,5-benzene (mCP):MoO₃ (20 wt.%, 10 nm)/mCP (30 nm)/Host:FIrpic (7 wt.%, 20 nm)/1,3,5-tri(m-pyrid-3-yl-phenyl) benzene (TmPyPB, 40 nm)/LiF (1 nm)/Al (100 nm), all of which display maximum external quantum efficiencies (EQEs) exceeding 20%. The DCPPO-based device reaches the highest EQE of 27.5%, the maximum luminance of 14070 cd m⁻², and the lowest efficiency roll-off of 22.2% from 1 to 10 mA cm⁻², which is among the best-performing FIrpic-based PHOLEDs without using any light extraction method.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) are becoming a new focus in flat or flexible panel display and solid-state lighting. Phosphorescent OLEDs (PHOLEDs), which promise an internal quantum efficiency of up to 100%, have been considered as the ultimate energy-saving technology.¹⁻³ So far the best-performing PHOLEDs are based on noble transition metal (i.e. iridium and platinum) complexes. Despite the fact that extensive progress has been achieved in PHOLEDs, the realization of blue ones with high efficiency remains a challenge.⁴⁻⁷

It has been proved that the selection of proper materials for each layer is very important for achieving highly efficient PHOLEDs.⁸ In particular, the design of host material plays a crucial role due to the following urgent demands: i) high triplet energy level $(E_{\rm T})$ for efficient energy transfer to the guest; ii) suitable energy levels of the frontier molecular orbitals (FMOs), i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), for better charge injection to lower the driving voltage; iii) balanced electron and hole transport ability to extend the recombination zone for low efficiency roll-off; iv) excellent evaporation ability for the vacuum deposition method for OLEDs' fabrication and high glass transition temperature (T_g) to increase morphological stability for lengthening the device lifetime. Moreover, the facile and inexpensive characters of the host materials are also important for the future commercialization of PHOLEDs, especially in the next-generation, largearea solid-state lighting market.

To meet the requirements of excellent host materials, the ambipolar donor (D)–acceptor (A) structure host materials are widely studied. For instance, carbazole (as a donor) and phosphine oxide (as an acceptor) are chosen as building blocks for the host materials since they are reported as efficient hole and electron transporting moieties with suitable FMO energy levels.^{4, 5, 8-21} In many cases, the phenylene moiety is needed as a spacer between the donor and acceptor for excellent hosts with a classical D- π -A structure, such as MPO12⁹, BCPO⁸ and TCTP¹⁰, with either 1, 2 or 3 carbazole subunits linked to the phenyl rings of a triphenylphosphine oxide core, respectively. All of these materials could act as excellent hosts for blue PHOLEDs, showing high external quantum efficiencies (EQEs) of 14.3%¹⁷, 23.5% and 15.9%, respectively. Intriguingly, Adachi group designed a D-A compound by directly linking the donor (a carbazole moiety) and acceptor (diphenylphosphine oxide) without the phenylene spacer. Compared to the corresponding D- π -A material (MPO12), this D-A compound showed similar high $E_{\rm T}$ while deeper HOMO energy levels, result in a better-performing blue PHOLED with a maximum EQE of 19.7%.17 Moreover, another D-A compound, dicarbazolylphenylphosphine oxide (DCPPO), was recently reported as an efficient host material for bis(3,5difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium (FIrpic) either by thermal evaporation²⁰ or wet-processing²² method, with maximum EQEs up to 16.5%.



Scheme 1. Synthetic routes of DCPP, DCPPO, TCP, and TCPO.

Based on aforementioned background, two compounds dicarbazolylphenylphosphine (DCPP) and tricarbazolylphosphine (TCP) were synthesized by direct linking carbazole and phosphine groups via a one-step reaction of carbazole and dichlorophenylphosphine or trichlorophosphine, and another two compounds DCPPO and tricarbazolylphosphine oxide (TCPO) were obtained through the one-step oxidation of DCPP and TCP with high yields exceeding 90%. Though the compounds DCPP and TCP have been reported as the ligands to construct Rh/Pd complexes²³, or with ultra-long phosphorescence²⁴, and DCPPO as an efficient host material for FIrpic, the performance of these four compounds as correlative host materials in OLEDs have never been completely studied and compared, especially considering that the oxidation of phosphine to phosphine oxide may easily improve the electron mobility and tune the bipolar property of the host matrix. After systematically study, it is demonstrated that the four compounds showed high $E_{\rm T}$ up to 3.0 eV, tunable carrier transport ability, suitable HOMO and LUMO energy levels, and excellent thermal stability. Furthermore, PHOLEDs based on the classic blue phosphorescent emitter FIrpic²⁵ were constructed with a simple structure adopting these four host materials. All of the devices display the maximum EQEs exceeding 20%, indicating these compounds could act as efficient host matrices for FIrpic. Especially, TCPO, firstly reported here, is a novel host material for blue PHOLEDs with maximum EQE up to 22%. The DCPPO-based device reached the highest EQE of 27.5%, the highest luminance of 14070 cd m⁻², and the lowest efficiency roll-off of 22.2% from 1 to 10 mA cm⁻².

2. RESULTS AND DISCUSSIONS

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2.1. Synthesis. The synthetic routes and chemical structures of DCPP, DCPPO, TCP, and TCPO are depicted in Scheme 1. DCPP and TCP were synthesized through a substitution reaction of carbazole and dichlorophenylphosphine or trichlorophosphine with high yields of 80% and 61%, respectively. DCPPO and TCPO could be obtained through the oxidization of DCPP and TCP by H_2O_2 with extremely high yields of 90% and 97%, respectively. After recrystallization, all the compounds were subsequently underwent thermal gradient sublimation twice. Their characterization details (¹H and ³¹P NMR spectroscopy and elemental analysis) are presented in the Experimental Section.

2.2. Crystal Structures and Molecular Interactions. The crystals of the four compounds were obtained by vacuum thermal sublimation and the structures were confirmed by single-crystal X-ray diffraction (XRD) analysis. All of the crystallographic data are available from the Cambridge Crystallographic Data Centre (CCDC) with numbers of 1554053,



Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing of molecular structures and π - π stacking interactions at 50% probability level. a) The π - π stacking of DCPP, b) 3 types of π - π stacking of DCPPO, the molecular structures of c) TCP and d) TCPO. All hydrogen atoms have been omitted for clarity.

1554055, 1554056, and 1554057.

For all compounds, the phosphine centers form tetrahedral geometries and they are surrounded by aromatic groups with propeller-like conformations (Figure 1). As shown in Figure 1a, there is only one type of π - π stacking interaction in the crystal of DCPP, while three types of π - π stacking in DCPPO crystal are observed (Figure 1b). Unlike DCPP and DCPPO, π - π stacking is suppressed in the crystals of TCP and TCPO, which could ascribe to larger intramolecular steric hindrance caused by three carbazoles. The carbazole groups squeeze in TCP or TCPO molecules, inhibiting the face-to-face interactions between carbazoles of adjacent molecules.

2.3. Photophysical Properties. The UV-Vis absorption and photoluminescence spectra of DCPP, DCPPO, TCP, and TCPO are recorded to study their photophysical properties (Figure 2a). The corresponding optical absorption data and calculated optical band gaps (E_g) are listed in Table 1.



Figure 2. a) UV-Vis absorption and photoluminescence spectra in CH_2Cl_2 solution (1×10⁻⁵ mol L⁻¹) at room temperature, b) Photoluminescence spectra in solid films and absorption of FIrpic in CH_2Cl_2 solution (1×10⁻⁵ mol L⁻¹) at room temperature, and c) Photoluminescence spectra in 2-MeTHF solution (1×10⁻⁵ mol L⁻¹) at 77 K of DCPP, DCPPO, TCP, and TCPO.

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Figure 3. a) Thermal gravimetric analysis, b) heat flow curves, and c) differential scanning calorimetry curves of DCPP, DCPPO, TCP, and TCPO.

| Table 1. Photop | hysical, electrochem | ical and thermal p | properties of the | four compounds. |
|-----------------|----------------------|---------------------------|-------------------|-----------------|
|-----------------|----------------------|---------------------------|-------------------|-----------------|

| Material | $\lambda_{max, abs.}{}^{a)}$ | $\lambda_{max, fl.}{}^{b)}$ | $\lambda_{max, phos.}^{c)}$ | $E_{ m g}{}^{ m d)}$ | $E_{\rm T}^{\rm e)}$ | HOMO ^{f)} | LUMO ^{g)} | T _{eva} ^{h)} | $T_{ m g}$ |
|----------|------------------------------|-----------------------------|-----------------------------|----------------------|----------------------|--------------------|--------------------|--------------------------------|------------|
| | [nm] | [nm] | [nm] | [eV] | [eV] | [eV] | [eV] | [°C] | [°C] |
| DCPP | 290 | 354 | 409 | 3.70 | 3.03 | 5.93 | 2.23 | 341 | 75 |
| DCPPO | 286, 256 | 354 | 409 | 3.88 | 3.03 | 6.33 | 2.45 | 366 | 80 |
| TCP | 289 | 344 | 415 | 3.70 | 2.99 | 5.94 | 2.24 | 373 | 89 |
| ТСРО | 284, 257 | 340 | 412 | 3.92 | 3.01 | 6.10 | 2.18 | 386 | / |

^{a)} The maximum absorption wavelength, measured in CH₂Cl₂ (1×10^{-5} mol L⁻¹) at room temperature; ^{b)} The maximum fluorescent emission peak, measured in CH₂Cl₂ (1×10^{-5} mol L⁻¹) at room temperature; ^{c)} The maximum phosphorescent emission peak, measured in 2-MeTHF (1×10^{-5} mol L⁻¹) at 77 K; ^{d)} Deduced from the corresponding absorption edges of the spectra; ^{e)} Deduced from the corresponding 0–0 transition bands of the phosphorescence spectra; ^{f)} Deduced from the oxidation potentials of the compounds; ^{g)} Calculated from the HOMO energy levels and the corresponding optical band gaps; ^{h)} Evaporation temperature under nitrogen.

A couple of characteristic absorption peaks were observed in the range of 270–340 nm at room temperature with molar extinction coefficients between 3000-16000 M⁻¹ cm⁻¹, which can be assigned to the π – π * and n– π * transitions of the carbazole moiety of the molecules.^{26, 27} The optical absorption edges of DCPP and TCP are almost the same (335 nm), indicating no significant electronic interactions between the carbazole or/and phenyl groups. The strong electron-withdrawing characteristic of the P=O group leads to noticeable blue shifts for the spectra of DCPPO and TCPO, with absorption edges moving from 335 nm to 320 nm and 316 nm, respectively.

In the fluorescence spectra (Figure 2a), the main peaks for DCPP and DCPPO are located at 354 nm with two shoulder emission peaks around 341 nm and 371 nm, respectively. For TCP and TCPO, the main peaks are blue-shifted to 344 nm and 340 nm, respectively. In addition, the emission spectra for the solid films of the four compounds and the absorption of FIrpic are presented in Figure 2b. The main peaks of DCPP, DCPPO, TCP and TCPO films are red-shifted to 397, 385, 375 and 350 nm, respectively, while the fine structure of the peaks disappears. It should be noted that TCP and TCPO show less red shift emission maximum in solid compared to DCPP and DCPPO, which may arise from suppressed π - π interaction in TCP and TCPO as mentioned in the aforementioned structures and interactions analysis. The emission peaks of the host materials could well overlap with the absorption spectrum of FIrpic, suggesting efficient Förster resonance energy transfer from the host materials to FIrpic.

The phosphorescence spectra (Figure 2c) of the four compounds were measured in 2-methyltetrahydrofuran (2-MeTHF) solution (1×10^{-5} mol L⁻¹) at 77 K. Similar phosphorescence spectra were observed in the range of 400-500 nm for the four compounds (the emission peaks around 340–400 nm can be assigned to fluorescence emission, with lifetimes of 6.6, 6.1, 10.6 and 10.6 ns for DCPP, DCPPO, TCP and TCPO, respectively). According to the 0–0 transition bands around 410 nm in their phosphorescent spectra, the $E_{\rm T}$ were calculated to be an identical 3.0 eV (Table 1). The high $E_{\rm T}$ can be attributed to the insulated carbazole moieties.

2.4. Thermal Properties. The thermal stability of the host material is vital for achieving high-performance and long-life optoelectronic devices. Thermal gravimetric analyses (TGA) demonstrated that all of the compounds possess good evaporation property and stability, which is important for vapor deposition method in OLED fabrication. As depicted in Figure 3a, the four compounds can be evaporated in the range of 340-390 °C without any decomposition. The heat flow curves (Figure 3b) suggest that these materials melt before evaporation, and the melting points (T_m) being 225 °C, 232 °C, 307 °C and 363 °C for DCPP, DCPPO, TCP and TCPO, respectively. High T_{g} is also indispensable for increasing morphological stability of the host materials to lengthen the device lifetime, and hence the $T_{\rm g}$ of DCPP, DCPPO and TCP were investigated by differential scanning calorimetry (DSC, Figure 3c) and described in Table 1. However, the $T_{\rm g}$ of TCPO could not be observed during several heating-cooling cycles. Based on the thermal properties, it is found that more rigid carbazole moiety endows TCP and TCPO with higher molecular weights and better thermal stability. Moreover, the oxidation of the phosphine also improves the thermal stability because of enhanced molecular polarity and weight. Overall, the thermal stabilities of all the four compounds are considerably excellent for device fabrication.

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Figure 4. a) Cyclic voltammetry curves and b) Experimental (blue) and DFT calculated (red) HOMOs, LUMOs of the molecules.

2.5. Frontier Molecular Orbital Studies. Cyclic voltammetry was employed to investigate the electrochemical properties of the four compounds and evaluate their HOMO energy levels. The oxidation process was conducted in degassed CH₂Cl₂ with ferrocene (Fc) as the internal reference.²⁸ The HOMO energy levels were estimated from the oxidation potentials (Figure 4a) to be 5.93, 6.33, 5.94, and 6.10 eV for DCPP, DCPPO, TCP, and TCPO, respectively, using the empirical formula reported in literature.²⁸ The LUMO energy levels were determined from their HOMO energy levels and optical band gaps calculated from their absorption spectra, which are 2.23, 2.45, 2.24, and 2.18 eV for DCPP, DCPPO, TCP, and TCPO, respectively. The HOMO (~ 5.9 eV) of DCPP and TCP is consistent to that of carbazole $(5.8 \text{ eV})^{18}$, while the strong electron-withdrawing phosphine oxide groups remarkably lower the FMOs of DCPPO and TCPO, especially for their HOMOs. These data suggest that the FMOs of the four compounds could fit well with plenty of common charge transport materials, such as mCP (HOMO = 5.9 eV) and TmPvPB (LUMO = 2.7 eV).

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Density functional theory (DFT) calculations were employed to investigate these compounds for a deeper insight into their electronic properties. B3LYP/6-31G* was chosen to optimize their geometry structures and calculate their FMO energy levels. The electron density distributions and energy levels of the FMOs are displayed in Figure 4b. The FMO distributions of DCPP are partly separated, while those of DCPPO are divided much more clearly. For these two molecules, the HOMOs are mainly located on the carbazole groups, and the LUMOs are centralized on the phenylphosphine or phenylphosphine oxide groups. In contrast, the HOMOs and LUMOs of TCP and TCPO are distributed around the whole molecules. These results indicate that DCPPO is a donor-acceptor molecule with ambipolar property, which may have more balanced carrier transport capability.

2.6. Electroluminescence Properties. To study the potential of the four compounds as host matrices for blue PHOLEDs, devices were fabricated with a structure (Figure 5a) of ITO/MoO₃ (1 nm)/*N*,*N*'-dicarbazolyl-3,5-benzene (mCP): MoO₃ (20 *wt*.%, 10 nm)/mCP (30 nm)/Host:FIrpic (7 *wt*.%, 20 nm)/1,3,5-tri(*m*-pyrid-3-yl-phenyl) benzene (TmPyPB, 40 nm)/LiF (1 nm)/Al (100 nm). The energy levels and structures of these materials are exhibited in Figure 5b and Figure 5c, respectively.



Figure 5. a) The schematic structure of fabricated PHOLEDs; b) the HOMOs, LUMOs, E_T levels, and c) the molecular structures of the compounds used in the devices.



Figure 6. a) Electroluminescence spectra for different OLEDs at 1000 cd m⁻²; b) Current density–voltage–luminance (J–V–L) characteristics of the devices; c) power efficiency-current density-external quantum efficiency (PE-J-EQE) of the devices.

A 1-nm-thick layer of MoO₃ was used to modify the work function of ITO to enhance hole injection. A 10-nm layer of mCP ($E_T = 2.9 \text{ eV}$) was doped by 20 wt. % MoO₃ to enhance hole injection,^{6, 29} followed by another 30-nm pristine mCP as the hole transporting layer. TmPyPB $(E_T = 2.8 \text{ eV})^{30}$ acted as the electron transporting layer as well as the hole blocking layer because of its low-lying HOMO level. As shown in Figure 5b, the HOMO levels of the hosts are about 0.4-0.8 eV higher than that of TmPyPB. As a result, holes can be effectively confined within the emitting layer (EML). Moreover, the chosen materials all possess higher $E_{\rm T}$ than FIrpic ($E_{\rm T}$ = 2.65 eV) to confine triplet excitons within the EML. The performance of the devices based on these host materials is summarized in Figure 6. All PHOLEDs exhibited characteristic sky-blue emission from FIrpic without any visible emission from the host materials (Figure 6a), indicating sufficient energy transfer from the host to the dopant. The current densityvoltage-luminance (J-V-L) characteristics are shown in Figure 6b. The turn-on voltages (V_{on}) of the devices are around 3.27-3.47 V. We found that the V_{on} increases as the HOMO level of the corresponding host matrix decreases. This phenomenon reveals that the V_{on} partly depends on the hole injection barrier from mCP to the host materials. At the same voltage, the devices with tri-substituted carbazole hosts (TCP or TCPO) gave higher current densities than those of the corresponding bi-substituted carbazole hosts (DCCP or DCCPO). At relative low driving voltages (lower than 5.5 V), the luminances are consistent with the current densities of the four devices, while the maximum luminances of DCPP- and TCPbased devices are much lower than those of the DCPPO- and TCPO-based devices. Figure 6c exhibits the power efficiencycurrent density-external quantum efficiency (PE-J-EQE) curves of the devices. The maximum EQEs of all devices exceeded 20%, demonstrating that all the four hosts are suitable for FIrpic-based blue PHOLEDs. Additionally, the perfor-



Considering that the vital parameters, such as $E_{\rm T}$, FMO energy levels and thermal properties, are similar for the four host materials, the variation in device performance may arise from the different ambipolar charge mobilities of the compounds. The hole or electron-only devices were fabricated to evaluate the charge mobilities of the four compounds. Electron-only devices ITO/BCP (Bathocuproine, 10 nm)/Host (30 nm)/BCP (10 nm)/LiF (1 nm)/Al (100 nm) were fabricated to characterize the electron transport abilities of these materials. The current densities of the DCPPO- and TCPO-based devices are higher than those based on DCPP and TCP (Figure 7a), which indicates that the electron transporting abilities are significantly enhanced after the oxidation of the phosphines. Additionally, the higher current density of the DCPPO-based device comparted to the TCPO-based one reveals that the phenyl group is critical to constructing the acceptor moiety in a molecule to enhance the electron transportation. The hole mobilities of the four hosts were characterized by corresponding hole-only devices with a structure of ITO/MoO3 (10 nm)/host (60 nm)/MoO₃ (10 nm)/Al (100 nm). As shown in Figure 7b, DCPP showed the best hole transporting ability (ignoring the hole injection barrier differences among the four compounds). Moreover, the hole transport abilities are weakened by the oxidation of phosphines. These results clearly indicate that the oxidation turn the hole-dominated carbazole phosphine into the bipolar materials.



Figure 7. The current density-voltage curves of a) electron- and b) hole- only devices.

| Table 2. Device performances of the blue PHOLEDs with the four different host mater | ials. |
|---|-------|
|---|-------|

| Device Von [V] | $V_{ m on}$ | $V_{\rm on} = L_{\rm max}^{a)}$ [V] [cd m ⁻²] | PE _{max} ^{b)} [lm W ⁻¹] | CE _{max} ^{c)} [cd A ⁻¹] | EQE [%] | | | | Roll-off ^{d)} | CIE ^{e,f)} |
|-------------------|-------------|--|--|--|---------|---------------------------|----------------------------|----------------------------|------------------------|---------------------|
| | [V] | | | | max | @1 mA cm ⁻² | @10 mA cm ⁻² | @20 mA cm ⁻² | [%] | [x, y] |
| DCPP | 3.27 | 1893 | 32.7 | 38.5 | 20.2 | 15.6 | 7.7 | 4.6 | 50.6, 70.5 | 0.15, 0.32 |
| DCPPO | 3.47 | 14070 | 42.7 | 53.0 | 27.5 | 22.5 | 17.5 | 14.7 | 22.2, 34.7 | 0.15, 0.32 |
| ТСР | 3.27 | 4596 | 34.3 | 39.2 | 20.4 | 18.0 | 12.1 | 8.5 | 32.8, 52.8 | 0.15, 0.32 |
| ТСРО | 3.31 | 13020 | 38.0 | 43.6 | 22.0 | 17.1 | 12.3 | 10.4 | 28.1, 39.2 | 0.15, 0.33 |

^{a)} Maximum luminance; ^{b)} Maximum power efficiency; ^{c)} Maximum current efficiency; ^{d)} From 1 mA cm⁻² to 10 mA cm⁻² and 1 mA cm⁻² to 20 mA cm⁻²; ^{e)} Value at 1000 cd m⁻²; ^{f)} Commission Internationale de l'Eclairage color coordinates.

Based on the study on electron-only and hole-only devices, it could be deduced that DCPP and TCP are hole-dominated materials, thus unbalanced carrier transport is expected to occur in the EML of their corresponding devices under high current densities. The excessive hole transport will push the recombination zone close to the interface of emission layer and electron transport layer, leading to strong triplet-triplet annihilation in the narrow exciton recombination zone.^{31, 32} As a result, the phosphine-based devices exhibited lower maximum luminance and much more severe efficiency roll-off as compared to their phosphine oxide-based counterparts. The promoted electron mobilities and diminished hole mobilities of DCPPO and TCPO can balance carrier transport and thus expand the exciton recombination zone, resulting in brighter luminance and lower efficiency roll-off. With the greatest electron mobility and highly balanced carrier transport of DCPPO, its corresponding device displayed the best EQE of 27.5% and the lowest efficiency roll-off of 22.2%.

3. CONCLUSION

Four host compounds, DCPP, DCPPO, TCP and TCPO, were synthesized by only one or two steps with high yields. All of them possess high $E_{\rm T}$, suitable FMO energy levels and excellent thermal stabilities, making them favorable for the manufacturing of blue PHOLEDs. We found that the charge mobility of the host materials can be modulated by the oxidation of phosphine. Compared to DCPP and TCP, DCPPO and TCPO showed improved electron mobility while retaining the high $E_{\rm T}$ and good hole mobilities, resulting in much more balanced carrier transportation for decreased efficiency roll-off. DCPPO provided its FIrpic-based device with the highest efficiencies, i.e. maximum current efficiency of 53.0 cd A⁻¹, power efficiency of 42.7 lm W⁻¹, and EQE of 27.5%, and the lowest efficiency roll-off of 22.2% from 1 to 10 mA cm⁻², which are among the best-performing FIrpic-based blue PHOLEDs without using any light extraction method.33-36

4. EXPERIMENTAL SECTION

General. Chemicals were received from commercial resources and used as received. Tetrahydrofuran (THF) was additionally dried over sodium and distilled. Reactions for preparing DCPP and TCP were carried out using Schlenk-line techniques under a pure dry nitrogen atmosphere, while these for synthesizing of DCPPO and TCPO were performed under air. The four materials underwent gradient sublimation (~ 10⁻⁵ Pa) before any characterization and device fabrication. ³¹P and ¹H NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer. Elemental analyzes were performed on a Vario EL instrument. Synthesis of dicarbazolylphenylphosphine (DCPP). A 2.5 M hexane solution of n-BuLi (20.0 mL, 50.0 mmol) was added dropwise to a stirred tetrahydrofuran-hexane solution (1:1, 200 mL) of carbazole (8.35 g, 50.0 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for two hours. Hexane was added to precipitate a white powder, which was isolated by filtration, washed with hexane and then dissolved in THF (200 mL). PhPCl₂ (4.48 g, 25.0 mmol) was added dropwise and the reaction mixture was stirred overnight. The solution was passed through a silica column and the solvent was evaporated under reduced pressure. The resulting white solid was recrystallized from acetone. Yield: 8.82 g (80%). ³¹P NMR (500 MHz, CDCl₃): δ 52.10 (s). ¹H NMR (500 MHz, CDCl₃): δ 7.99-8.00 (d, 4H, J = 6.5 Hz), 7.56-7.58 (d, 4H, J = 7.5 Hz), 7.46-7.49 (t, 3H, J = 7.0, 8.5Hz), 7.38-7.41 (t, 2H, J = 7.5, 7.0 Hz), 7.21-7.27 (m, 8H). Calc. for C₃₀H₂₁N₂P: C, 81.80; H, 4.81; N, 6.36. Found: C, 81.89; H, 4.80; N, 6.41.

Synthesis of dicarbazolylphenylphosphine oxide (DCPPO). DCPP (4.40 g, 10.0 mmol), CH₂Cl₂ (100 mL), and H₂O₂ (30%, 20 mL) were stirred overnight at room temperature. The organic layer was separated and washed with water and brine. The extract was evaporated to dryness affording a white solid, which was further purified by recrystallization and gradient sublimation. Yield: 4.12 g (90%). ³¹P NMR (500 MHz, CDCl₃): δ 8.45 (s). ¹H NMR (500 MHz, CDCl₃): δ 8.00-8.02 (d, 4H, *J* = 7.5 Hz), 7.80-7.84 (q, 2H, *J* = 8.0, 6.5, 8.0 Hz), 7.67-7.70 (t, 1H, *J* = 7.5, 7.5 Hz), 7.47-7.51 (m, 2H), 7.24-7.27 (t, 4H, *J* = 7.0, 8.5 Hz), Calc. for C₃₀H₂₁N₂OP: C, 78.94; H, 4.64; N, 6.14. Found: C, 78.90; H, 4.61; N, 6.15.

Synthesis of tricarbazolylphosphine (TCP). The synthetic procedure of TCP is similar to that of DCPP, using carbazole (8.35 g, 50.0 mmol), n-BuLi (20.0 mL, 50.0 mmol), and PCl₃ (2.29 g, 16.7 mmol). Yield: 5.42 g (61%). ³¹P NMR (500 MHz, CDCl₃): δ 76.84 (s). ¹H NMR (500 MHz, CDCl₃): δ 8.05-8.06 (d, 6H, *J* = 7.5 Hz), 7.23-7.26 (t, 6H, *J* = 7.5, 7.5 Hz), 7.16-7.18 (d, 6H, *J* = 8.0 Hz), 7.10-7.13 (t, 6H, *J* = 7.0, 8.5 Hz). Calc. for C₃₆H₂₄N₃P: C, 81.65; H, 4.57; N, 7.93. Found: C, 81.56; H, 4.56; N, 7.95.

Synthesis of tricarbazolylphosphine oxide (TCPO). The synthetic procedure of TCPO is similar to that of DCPPO, a mixture of TCP (2.65 g, 5.0 mmol), CH₂Cl₂ (50 mL), and H₂O₂ (30%, 10 mL) was stirred for 36 h. Yield: 2.65 g (97%). ³¹P NMR (500 MHz, CDCl₃): δ -13.06 (s). ¹H NMR (500 MHz, CDCl₃): δ 8.04-8.05 (d, 6H, *J* = 7.5 Hz), 7.26-7.29 (t, 6H, *J* = 7.0, 7.0 Hz), 7.05-7.12 (m, 12H). Calc. for C₃₆H₂₄N₃OP: C, 79.25; H, 4.43; N, 7.70. Found: C, 79.33; H, 4.45; N, 7.76.

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Photophysical Measurement. UV-Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Florescence and low temperature phosphorescence spectra were carried out on an Edinburgh Analytical Instruments FLS920 spectrophotometer.

Cyclic Voltammetry Measurements. Cyclic voltammetry was measured in nitrogen-purged CH_2Cl_2 solution at room temperature with a CHI600C voltammetric analyzer and tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl wire pseudo-reference electrode.

Thermal Properties Measurements. Thermal gravimetric analysis was undertaken with a Q100DSC instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 15 °C min⁻¹ from 25 to 600 °C. Differential scanning calorimetry was performed on a Q600SDT instrument unit at a heating rate of 15 °C min⁻¹ from 25 to 280 °C under nitrogen. The glass transition temperature was determined from the second heating scan.

Theoretical Calculations. For calculation of HOMO and LUMO energy levels, density functional theory (DFT) calculations were performed for optimized molecular structures at the B3LYP/6-31G* levels, respectively, using a Gaussian suite of programs (Gaussian 09, Revision A.01).

Device fabrication and testing. MoO₃, mCP and TmPyPB were purchased from Lumtec. BCP was purchased from Xi'an Polymer Light Technology Corp. Patterned indium tin oxide (ITO) anode is commercially available with a sheet resistance of 14 Ω square⁻¹ and 80-nm thickness. Before loading into a deposition chamber, the ITO substrate was cleaned with detergent, deionized water, acetone and ethanol. The organic and metal layers were deposited in different vacuum chambers with a base pressure better than 8×10^{-5} Pa. The active area for all devices is 4 mm². The devices were capsulated in a glove box under a nitrogen atmosphere. All electrical testing and optical measurements were performed under ambient conditions. The EL spectra, current density-voltage-luminance (J-V-L) and EQE characteristics were measured by computer controlled Keithley 2400 source meter and absolute EQE measurement system (C9920-12, Hamamatsu Photonics) with the photonic multichannel analyzer (PMA-12, Hamamatsu Photonics).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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