Elevating the Triplet Energy Levels of Dibenzofuran-Based Ambipolar Phosphine Oxide Hosts for Ultralow-Voltage-Driven Efficient Blue Electrophosphorescence: From D-A to D $-\pi$ -A Systems

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Abstract: A series of donor (D)- π -acceptor (A)-type phosphine-oxide hosts $(\mathbf{DBF}_{x}\mathbf{POPhCz}_{n})$, which were composed of phenylcarbazole, dibenzofuran (DBF), and diphenylphosphineoxide (DPPO) moieties, were designed and synthesized. Phenyl π -spacer groups were inserted between the carbazolyl and DBF groups, which effectively weakened the charge transfer and triplet-excited-state extension. As the result, the first triplet energy levels (T_1) of **DBF**_x**POPhCz**_n are elevated to about 3.0 eV, 0.1 eV higher than their D-A-type analogues. Nevertheless, the electrochemical analysis and DFT calculations demonstrated the ambipolar characteristics of **DBF**_x**POPhCz**_n. The phenyl π spacers hardly influenced the frontier molecular orbital (FMO) energy levels and the carrier-transporting ability of the materials. Therefore, these D $-\pi$ -A systems are endowed with higher T₁ states, as well as comparable electrical properties to D–A systems. Phosphorescent blue-light-emit-

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Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have promising applications in the next generation of flatpanel displays^[1] and in solid-state lighting,^[2] owing to their advantages in terms of energy saving, such as their high internal quantum efficiencies (approaching 100%), in devices in which the host material is one of the determinants of device performance.^[3] During electroluminescent (EL) processes, the hosts in the emitting layers (EMLs) of dopingtype PHOLEDs have three functions: 1) Suppressing multiparticle quenching effects through the uniform dispersion of herited the ultralow driving voltages (2.4 V for onset, about 2.8 V at 200 cdm⁻², and < 3.4 V at 1000 cdm⁻²) but also had much-improved efficiencies, including about 26 cd A⁻¹ for current efficiency, 30 Lm W⁻¹ for power efficiency, and 13% for external quantum efficiency, which were more than twice the values of devices that are based on conventional unipolar host materials. This performance makes **DBFDPOPhCz**_n among the best hosts for ultralow-voltage-driven blue PHO-LEDs reported so far.

ting diodes (PHOLEDs) that were

based on **DBF**_x**POPhCz**_n not only in-

phosphorescent dopants; 2) facilitating and balancing carrier injection and transportation; and 3) transferring energy to the dopants.^[4] Therefore, an eligible host materials should be both optically and electrically active.^[5] However, for blue-light-emitting PHOLEDs, the optical and electrical properties of the hosts often contradict each other and rarely support good optoelectronic performance simultaneously.^[6] The origin of this problem is the similar effects of these modification approaches on the singlet (S_1) and triplet excited energy levels (T_1) .^[7] In this sense, it is rather difficult to achieve exothermic host-guest energy transfer and improved carrier-injecting/transporting ability at the same time, because the former requires a high enough T_1 state in the hosts (approaching 3.0 eV for conventional blue phosphor [iridium(III)bis(4,6-(difluorophenyl) pyridinato-N,C2)picolinate] (FIrpic)),^[8] whereas the latter should originate from a relatively low S₁ state in the hosts to make their frontier molecular orbital (FMO) energy levels fit to those of the adjacent carrier-transporting layers.^[9] Obviously, the selective modulation of the excited energy levels of a host is the key point in facing this great challenge.^[10]

Although some effective strategies, such as *meso*-,^[11] insulating,^[8,12] and twisted linkages,^[13] have been used to construct hosts with high T_1 states, these hosts still cannot provide enough electrical performance. Therefore, there are only few FIrpic-based devices that have low driving voltages

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of less than 3 V at 100 cd m⁻².^[9,12j,14] Recently, the success of ambipolar hosts for blue electrophosphorescence has pointed the way towards highly efficient hosts with high T₁ states and balanced carrier-transporting ability.^[9,11b,12g,1,13b,15] Ambipolar structures can support both hole and electron injection and transportation through electron-donating and electronwithdrawing groups, respectively.^[16] Thus, the electrical properties of a molecule can be conveniently tuned by incorporating different kinds and numbers of electrically active groups. Nevertheless, a strong donor-acceptor (D-A) interaction remarkably lowers the T1 state, owing to the formation of charge-transfer (CT) states.^[17] To solve this problem, one of the main strategies involves blocking the intramolecular interplay by insulating linkages, such as saturated Si^[12g] or C atoms.^[12i] We also found that, on the basis of indirect linkage through the C9 atom of fluorene, the interplay between hole-transporting carbazolyl and electron-transporting diphenylphosphine-oxide (DPPO) groups can be effectively suppressed to achieve ambipolar hosts with a preserved T₁ state of 3.0 eV.^[121] Both high EL efficiencies and efficiency stability were realized; however, the driving voltage at 100 cd m⁻² was over 3.5 V. This result implies that electrically inert saturated Si and C sites in the hosts are inferior in terms of carrier injection and transportation. Thus, we recently constructed a series of dibenzofuran (DBF)-based ternary hosts (DBF, POCz,) through short-axis and meso linkages (Scheme 1).^[9] Inspiringly, these hosts endowed their



Scheme 1. Design strategy and a structural comparison of **DBF**_x**POPhCz**_n and **DBF**_x**POCz**_n.

FIrpic-based PHOLEDs with extremely low driving voltages of less than 2.8 V at 100 cd m⁻², presumably owing to the use of active **DBF** groups instead of inert Si or C moieties to bridge the carbazolyl and DPPO groups. However, the weak CT between the directly linked **DBF** and carbazolyl groups still lowered the T₁ states (about 2.9 eV) and, consequently, resulted in lower EL efficiencies.

Until now, the determinants of the excited-state and electrical properties are still not very clear. The detailed influence of molecular structure and various effects on the photoelectrical performance of the hosts are still one of the most important issues in this field. Therefore, herein, we report the synthesis of another series of ternary carbazolyl–



DBF–DPPO hybrids through inserting phenyl groups between the carbazolyl and **DBF** moieties as π spacers to restrict the direct CT (Scheme 1), namely (2-(4-(9*H*-carbazol-9-yl)phenyl))-(6-diphenylphosphoryl)dibenzofuran

(DBFSPOPhCz), (2-(4-(9H-carbazol-9-yl)phenyl))-(4,6-bis-(diphenylphosphoryl))dibenzofuran (DBFDPOPhCz), and (2,8-bis(4-(9H-carbazol-9-yl)phenyl))-(4,6-bis(diphenylphosphoryl))dibenzofuran (DBFDPOPhCz₂), collectively named $\mathbf{DBF}_{x}\mathbf{POPhCz}_{n}$. As expected, although the additional phenyl groups increase the conjugation, the T₁ states of **DBF**_x**POPhCz**_n were elevated to about 3.0 eV, owing to the effective suppression of CT. Simultaneously, the ambipolar characteristics of **DBF**_x**POPhCz**_n endowed FIrpic-based devices with extremely low driving voltages (2.4 V for onset, < 2.8 V for 200 cd m⁻², < 3.4 V for 1000 cd m⁻²), which were the same as those of **DBF**, **POCz**, based devices, whilst the efficiencies of devices that were based on $DBF_rPOPhCz_n$ were dramatically improved by more than 30%. Our investigation not only exhibited the potential of **DBF**_x**POPhCz**_n as hosts for highly efficient low-voltage-driven PHOLEDs, but also clarified the negative influence of the CT states and extended conjugation on the T₁ states. This result can further direct the controllable tuning of molecular optoelectronic properties and the purposeful design of high-performance host materials.

Results and Discussion

Design and synthesis: It is common sense that extended conjugation can result in a simultaneous decrease of the S₁ and T₁ states, whilst the formation of low-energy CT states also induces instability of the T₁ state. Therefore, it seems that both of these features should be avoided when designing high-energy-gap hosts for blue electrophosphorescence. However, if bipolar structures were involved in hosts to enhance their electrical properties, the suppression of the negative influence of their potential CT states on the T₁ states becomes a serious problem. One immediate thought is the use of saturated linkers, such as aliphatic chains, to block the interplay between the donors and acceptors. However, the incorporation of inert insulated moieties would also decrease their electrical performance. Meier reported that π spacers can also weaken the interaction between donors and acceptors.^[17] However, π spacers would also increase the conjugation. Therefore, their introduction appears to present both positives and negatives. In fact, the answer to this quandary is to determine which of the CT excited state and extended conjugation has the main effect on the T_1 state. Obviously, the conclusion is significant for the purposeful design of ternary high-energy-gap host materials. Therefore, we designed three DBF-based ternary phosphine-oxide (PO) hosts $(DBF_xPOPhCz_n)$ in which carbazolyl groups act as donors and DPPO-substituted DBF groups act as acceptors with phenyl groups between them as π spacers. Thus, **DBF**_x**POPhC** z_n are D $-\pi$ -A-type structures, compared to D–A-type $\mathbf{DBF}_{x}\mathbf{POCz}_{n}$ (Scheme 1).



Scheme 2. Synthesis of $DBF_x POPhCz_n$; NBS = N-bromosuccinimide.

DBF_x**POPhC**_{z_n} was conveniently prepared from *o*-**DBFPPO**^[14b] or *o*-**DBFDPO**^[18] through a simple two-step procedure of bromination and Suzuki coupling, with a good total yield about 50% (Scheme 2). Structural characterization was established on the basis of MS, NMR spectroscopy, and elemental analysis.

Thermal and morphological properties: The thermal stability of **DBF**_x**POPhCz**_n was investigated by thermogravimetric analysis (TGA), which revealed a high temperature of decomposition ($T_d > 450$ °C; Figure 1 and Table 1). Along with the extension of conjugation, the T_d values of **DBFSPOPhCz**, **DBFDPOPhCz**, and **DBFDPOPhCz**₂ gradually increased to 467, 516, and 544 °C, respectively. Furthermore, compared with the corresponding **DBF**_x**POCz**_n

series,^[9] the incorporation of phenyl spacers into DBF, POPhCz, induced a remarkable increase in the $T_{\rm d}$ value (10-30°C). This increase is attributed to the stronger structural adjustability and the decreased volatility of the latter series. Their improved thermal stability makes device fabrication through vacuum evaporation more feasible. Differential scanning calorimetry (DSC) analysis showed that the melting points $(T_{\rm m})$ of DBFSPOPhCz.

Table 1. Physical properties of **DBF**_x**POPhCz**_n.

Host	Absorption [nm]	Emission [nm]	$\begin{array}{l} S_1{}^{[c]}\!/T_1{}^{[d]} \\ [eV] \end{array}$	$T_{\rm d}/T_{\rm m}/T_{\rm g}$ [°C]	RMS [nm]	HOMO/LUMO [eV]
DBFSPOPhCz	340, 328, 294, 273, 245 ^[a] 344, 330, 314, 298, 249 ^[b]	315, 370 ^[a] 387, 405, 427 ^[b]	3.89/2.98	467/253/ 165	0.711	$\begin{array}{c} -5.31/{-}1.31^{[e]} \\ -6.09/{-}2.84^{[f]} \end{array}$
DBFDPOPhCz	341, 329, 309, 293, 274, 247 ^[a]	407 ^[a]	3.54/2.97	516/311/ 156	0.751	$\begin{array}{c} -5.36/{-}1.44^{[e]} \\ -6.09/{-}2.87^{[f]} \end{array}$
DBFDPOPhCz ₂	345, 329, 313, 298, 254 ^[b] 340, 329, 293 345, 328, 297, 255 ^[b]	407 ^[0] 410 ^[a] 410 ^[b]	3.49/2.97	544/323/ 157	0.758	$-5.39/-1.53^{[e]}$ $-6.09/-2.93^{[f]}$

[a] In CH₂Cl₂ ($\times 10^{-6}$ mol L⁻¹); [b] in a film; [c] estimated according to the absorption edges; [d] calculated ac-

cording to the 0-0 transitions in the phosphorescence spectra; [e] DFT-calculated results; [f] calculated accord-

DBFDPOPhCz,

DBFDPOPhCz₂ were 253, 311, and 323 °C, respectively, whereas their glass-transition temper-

atures (T_g) were 165, 156, and 157 °C. Both the T_m and T_g values of **DBF_xPOPhCz**_n were lower than those of their parent molecule, **o-DBFDPO**, which should be attributed to decreased $\pi - \pi$ intermolecular interactions and the lower molecular rigidity, owing to the presence of phenylcarbazole moieties with a high degree of freedom, in **DBF_xPOPhCz**_n.

and

SEM and AFM images of vacuum-evaporated thin films of $DBF_xPOPhCz_n$ showed direct evidence of their solid-

state morphologies (Figure 2). **DBFSPOPhCz** revealed local aggregation in its SEM image, which could be ascribed to its least-bulky moieties and the smallest molecular volume among the **DBF_xPOPhCz**_n series. However, no aggregation and crystallization were observed in the SEM images of the bigger analogues, **DBFDPOPhCz** and **DBFDPOPhCz**₂. This result indicates that conjugated and sterically demanding host materials are advantageous, not only in terms of electri-

ing to the onset voltages of the redox peaks.



Figure 1. TGA curves of **DBF**_x**POPhCz**_n.



Figure 2. SEM (top) and AFM images (bottom) of vacuum-evaporated films of DBF_xPOPhCz_n.

cal performance, but also in terms of morphological stability. Nevertheless, AFM analysis showed that all of the films were rather smooth with root-mean-square (RMS) roughness of around 0.7 nm, which confirms the excellent filmforming ability of these host materials. These stable and high-quality amorphous films are very important for improving device performance by restricting the formation of defects in the EMLs or at the interfaces with adjacent layers.

Optical properties: The photophysical properties of $DBF_xPOPhCz_n$ were indicated from their UV/Vis and photoluminescence (PL) spectra as dilute solutions in CH₂Cl₂ $(1 \times 10^{-6} \text{ mol } \text{L}^{-1})$ and as thin films (Figure 3). Their absorption spectra can be divided into three main absorption bands, at 320–350, 270–320, and 220–270 nm. The $n \rightarrow \pi^*$ transitions of the DBF and carbazolyl moieties overlap in the range 320-350 nm, thereby revealing two peaks at about 329 and about 341 nm, respectively. Compared with its other two analogues, this absorption band of DBFDPOPhCz₂ becomes much stronger, in accord with its increased proportion of carbazolyl groups. The distinct absorption peaks at about 293 nm are attributed to the $\pi{\rightarrow}\pi^*$ transition of the carbazolyl groups, which are also superimposed with the peaks that originate from the $\pi \rightarrow \pi^*$ transition of the **DBF** groups (273, 283, and 309 nm). The third absorption bands, with peaks at about 250 nm, are ascribed to the $\pi \rightarrow \pi^*$ transitions of the phenyl groups in the DPPO moieties. There-



Figure 3. Top: absorption and FL spectra of **DBF**_x**POPhC**_{z_n} in CH₂Cl₂ (× 10^{-6} molL⁻¹, filled shapes) and in films (empty shapes). Bottom: phosphorescence spectra in CH₂Cl₂ (× 10^{-6} molL⁻¹) at 77 K after a decay of 300 µs.

fore, both the phenylcarbazole and **DBF** moieties provide the main contributions to the molecular excited energy levels. Furthermore, compared with the optical energy gaps (which correspond to the S_1 state) of *o***-DBFPPO** (3.89 eV) and *o***-DBFDPO** (3.63 eV), the introduction of one phenylcarbazole group into **DBFSPOPhCz** (3.54 eV) and

1388 ·

DBFDPOPhCz (3.49 eV) results in a decrease in the S_1 state of 0.35 and 0.14 eV, respectively, whilst the second phenylcarbazole in DBFDPOPhCz₂ (3.44 eV) induces a further decrease of 0.05 eV. Notably, the formation of a bipolar structure can dramatically lower the S₁ state by more than 0.14 eV. Then, each additional DPPO or phenylcarbazole group gives rise to a further decrease of 0.05 eV. Thus, through combining different kinds of carrier-transporting moieties and tuning the ratio of these functional groups, we can feasibly realize the controllable modulation of the S₁ energy levels. The peak position and shape of all of these bands in their absorption spectra in solution are completely preserved in the spectra in films, with negligible bathochromic shifts (less than 5 nm). This result further demonthe weak intermolecular interactions strates of $DBF_xPOPhCz_n$ in the solid state, as indicated in the AFM and SEM images (Figure 2).

The fluorescence (FL) emission spectrum of DBFSPOPhCz at room temperature as a dilute solution in CH₂Cl₂ consists of a duplicate peak at 350 and 370 nm. In film, this emission peak is located at 403 nm, with a bathochromic shift of 33 nm, which should be induced by aggregation, as shown in its SEM image (Figure 2). The FL emission spectra of DBFDPOPhCz and DBFDPOPhCz₂ show main peaks at 405 and 410 nm, respectively, which are red-shifted approximately 30 nm compared with that by of DBFSPOPhCz, mainly owing to their second DPPO groups. From DBFDPOPhCz to DBFDPOPhCz₂, the second phenylcarbazole group only induces a small red-shift of 5 nm. Nevertheless, it is noticeable that the solid-state emissions of DBFDPOPhCz and DBFDPOPhCz₂ are almost the same as those in solution, which further confirms their suppressed aggregation in their solid states, consistent with the results of the morphological investigation. Furthermore, the solid-state emissions of $DBF_xPOPhCz_n$ are very similar in shapes and range. Therefore, in their PHOLEDs, the singlet energy transfer to phosphorescent dopants should be also similar. The emissions of $DBF_xPOPhCz_n$ in films have wideranging overlap with the metal-to-ligand charge-transfer (MLCT) absorption bands of conventional blue, green, yellow, and red phosphors to support efficient Förest resonance energy transfer (FRET). The phosphorescence (PH) spectra of **DBF**_x**POPhC** z_n at 77 K, after a delay of 300 µs, were measured to determine their T₁ energy levels through an estimation from their $v_{0,0}$ transitions, which were identified as the highest-energy bands. We showed that the combined linkage strategy of meso- and short-axis substitution endowed **DBF**_x**POPhC** z_n with very similar T₁ energy levels (around 3.0 eV), which corresponded to about 415 nm (Figure 3 and Table 1), as shown by **DBF**_x**POC**z_n.^[9] More significantly, the D- π -A structures of **DBF**_x**POPhCz**_n elevate the T₁ level by more than 0.1 eV compared with the D-A-type $\mathbf{DBF}_{\mathbf{x}}\mathbf{POCz}_{\mathbf{n}}$ structures. Nevertheless, closer observation shows that the intensity of the v_{00} transition sharply decreases from DBFSPOPhCz to DBFDPOPhCz and DBFDPOPhCz₂. This situation is highly distinct from that of $\mathbf{DBF}_{x}\mathbf{POCz}_{n}$, in which the intensity of the $v_{0,0}$ transitions is almost constant, along with the extension of conjugation.^[9] This result means that, compared with D–A-type structures, D– π –A-type bipolar structures can indeed suppress the reduction effect of CT on the T₁ energy levels but, simultaneously, sacrifice the stability of the T₁ excited states.

DFT calculations: To determine the influence of the D $-\pi$ -A-type bipolar structure on their FMOs, density function theory (DFT) calculations were conducted with the Gaussian 03 package at the B3LYP level and the 6-31G* basis set (Figure 4). The HOMOs of **DBFSPOPhCz**, **DBFDPOPhCz**,



Figure 4. DFT calculations of the molecular configurations and molecular-orbital contours in the ground states and the spin-density distributions in the T_1 states of **DBF_xPOPhCz**_n.

and DBFDPOPhCz₂ are -5.306, -5.360, and -5.360 eV, respectively, 1.0 eV higher than those of o-DBFPPO and o-DBFDPO. Moreover, the calculated LUMOs of DBFSPOPhCz, DBFDPOPhCz, and DBFDPOPhCz₂ are -1.306, -1.442, and -1.534 eV, respectively, 0.1 eV lower than those of *o*-DBFPPO^[14b] and *o*-DBFDPO.^[18] This result shows that, owing to its electron-withdrawing effect, the second DPPO group in DBFDPOPhCz induces a decrease of 0.14 eV in the LUMO and a decrease of 0.054 eV in the HOMO. Therefore, the HOMO-LUMO energy gap (E_g) of DBFDPOPhCz is about 0.1 eV smaller than that of DBFSPOPhCz. The second phenylcarbazole in **DBFDPOPhCz₂** also lowers the LUMO by about 0.1 eV; however, it has no influence on the HOMO. As a result, the E_{σ} value of **DBFDPOPhCz**₂ is decreased by a further 0.1 eV. Furthermore, the two symmetrical phenylcarbazoles in DBFDPOPhCz₂ mainly contribute to the HOMO and HOMO-1, respectively, which are almost degenerate, with a very small energy difference (0.028 eV). Because their

A EUROPEAN JOURNAL

symmetrical configuration and small intramolecular energy gap are advantageous for carrier hopping between different molecules, DBFDPOPhCz₂ can be expected to show improved hole-transporting ability. Owing to their higher LUMOs and lower HOMOs, the E_{σ} values of DBFSPOPhCz, DBFDPOPhCz, and DBFDPOPhCz₂ are 0.1, 0.2, and 0.3 eV larger than those of their corresponding $\mathbf{DBF}_{x}\mathbf{POCz}_{n}$ analogues,^[9] respectively. This result reflects the fact that the phenyl π spacers can (at least partially) weaken the CT between the carbazolyl and DBF groups. Furthermore, the LUMO+1 levels of $DBF_xPOPhCz_n$ are mainly located on the DBF groups and on the phenyl groups of the phenylcarbazoles. This result is different to the situation of DBF_rPOCz_n , in that their LUMO+1 levels are mainly constituted of DPPO groups. On the other hand, the contribution of the **DBF** groups in **DBF**_x**POPhC** z_n to the HOMOs is smaller than in DBF_xPOCz_n . Therefore, the phenyl π spacers effectively suppress the interplay between the carbazolyl and **DBF** groups in **DBF**_x**POPhC** z_n .^[19]

The triplet states of **DBF**_x**POPhCz**_n were also optimized at the B3LYP level. The calculated T₁ states are 3.10, 3.06, and 3.17 eV, respectively, which are in accord with the results estimated from the PH spectra. The contours of the spin-density distributions (SDD) of the triplet states indicate that the T₁ states are absolutely localized on either the **DBF** or carbazolyl groups (see the Supporting Information, Figure S1). Therefore, the incorporation of phenyl π spacers can restrain the CT between the carbazolyl and **DBF** groups, without having a negative influence on the triplet states.

Carrier-injection/transportation properties: Cyclic voltammetry was performed to investigate the redox behavior of **DBF_xPOPhCz**_n (Figure 5). All of these compounds had two sets of oxidation peaks, which corresponded to the carbazolyl and **DBF** moieties, respectively. For **DBFSPOPhCz**, the first peak for the carbazolyl moiety was at 1.42 V, with an onset voltage of 1.31 V, thus corresponding to a HOMO of -6.09 eV, whereas the second group from **DBF** was at 2.28 V. Although the oxidation peaks of **DBFDPOPhCz**

shift to 1.49 and 2.41 V, respectively, its onset voltage is also at 1.31 V. However, owing to its additional phenylcarbazole group, **DBFDPOPhCz**₂ has two neighboring peaks from the carbazolyl groups at 1.66 and 1.81 V, which are in accord with the DFT calculations, whereas its DBF-based peak is at 2.35 V. Nevertheless, according to the onset voltage, its HOMO is also at -6.09 eV. Although DFT calculations showed that the **DBF** groups in **DBF**_x**POPhC**_{z_n} made slight contributions to the HOMOs, the same oxidation onset voltages of **DBF**_x**POPhCz**_n directly demonstrated the limited influence of the DPPO and DBF groups on the HOMOs. The DBF_xPOPhCz_n series all revealed similar reversible reduction peaks at around 2.2 V, which were ascribed to the DBF groups. The peak for **DBFSPOPhCz** was at -2.25 V, with an onset voltage of -1.94 V, which corresponded to a LUMO of -2.84 eV. With one more DPPO group, DBFDPOPhCz had a reduction peak at -2.08 V and an onset voltage of -1.91 V, which corresponded to a LUMO of -2.87 eV. Therefore, the second DPPO induced a small decrease in the LUMO of only 0.03 eV. However, the reduction peak of **DBFDPOPhCz₂** further shifted to -2.05 V, with an onset voltage of -1.85 V, which corresponded to a LUMO of -2.93 eV. This sequential lowering of the LUMO by 0.06 eV should be ascribed to the extension of conjugation by binding one more phenyl group onto DBF. These CV data are precisely consistent with those from the DFT calculations.

Next, we fabricated nominal single-carrier-transporting devices with the configurations ITO/MoO_x (2 nm)/4,4',4''tri(N-3-methylphenyl-N-phenylamino)triphenylamine (m-MTDATA):MoO_x (15 wt. %, 30 nm)/m-MTDATA (10 nm)/ [tris(phenylpyrazole)iridium] $([Ir(ppz)_3],$ 10 nm)/ 10 nm)/m-MTDATA **DBF**_r**POPhCz**_n $(40 \text{ nm})/[Ir(ppz)_3]$, (10 nm)/m-MTDATA:MoO_y (15 wt.%, $30 \text{ nm}/MoO_{x}$ (2 nm)/Al and Al/Cs₂CO₃ (1 nm)/4,7-diphenyl-1,10-phenanthroline (BPhen) $(40 \text{ nm})/\text{DBF}_x\text{POPhCz}_n$ (40 nm)/Bphen (40 nm)/Cs₂CO₃ (1 nm)/Al for hole-only and electron-only carriers, respectively, to investigate the carrier-transporting properties of $DBF_xPOPhCz_n$ (Figure 6). The current density (J) of a hole-only device that was based on DBFSPOPhCz was lower than that of a hole-only device that was based on



Figure 5. CV redox curves of $DBF_xPOPhCz_n$ in CH_2Cl_2 .



Figure 6. *I–V* characteristics of nominal hole-only (empty shapes) and electron-only devices (filled shapes) based on **DBF_xPOPhCz**_n.

DBFDPOPhCz, whereas DBFDPOPhCz₂ endowed its hole-only device with the highest J values (at the same voltages). In our previous report, we found that, for **DBF**_x**POC**_{z_n}, the J values of their hole-only devices were proportional to the number of carbazolyl groups and inversely proportional to the number of DPPO units.^[9] Furthermore, a symmetrical configuration is advantageous in carrier transportation. However, owing to the greater hindrance and higher number of degrees of freedom in phenylcarbazoles, the effect of molecular configuration becomes a determinant. Therefore, the hole-only J values of devices that were based on the



Scheme 3. Energy-level diagram of blue-, green-, yellow-, and red-light-emitting PHOLEDs and the molecular structures of the materials that were used.

more-symmetrical **DBFDPOPhCz** structure were higher than those based on **DBFSPOPhCz**. As the DFT calculations showed, although the DPPO groups enhanced the electron-injection ability of the compound, the **DBF** groups had strong electron-transporting ability. More peripheral groups in **DBFDPOPhCz**_n suppress the interaction between the **DBF** groups. This suppression is the main reason that **DBFSPOPhCz** endows its electron-only device with the highest J value. Thus, when the pendant functional groups have a strong steric effect, except for the inherent properties of electrically active moieties for carrier transportation, the molecular configuration also cannot be ignored.

CV analysis and the single-carrier-only *I–V* characteristics of **DBF**_x**POPhCz**_n showed that it had similar HOMO (about -6.1 eV) and LUMO levels (about -2.85 eV) and comparable carrier-transporting abilities to **DBF**_x**POCz**_n.^[9] Therefore, we believe that, although the incorporation of phenyl π spacers restrains the intramolecular CT, the carrier-injecting/transporting abilities and the ambipolar characteristics of **DBF**_x**POPhCz**_n are not weakened.

EL properties: The high T_1 levels (approaching 3.0 eV) and ambipolar characteristics of $DBF_xPOPhCz_n$ inspired us to fabricate their blue-light-emitting PHOLEDs with the configuration ITO/MoO_x (2 nm)/m-MTDATA:MoO_x (15 wt. %, 30 nm/m-MTDATA $(10 \text{ nm})/[Ir(ppz)_3]$ (10 nm)/host:FIrpic10 nm)/BPhen $(40 \text{ nm})/Cs_2CO_3$ (10 wt.%, (1 nm)/Al(100 nm), where MoO_x and Cs_2CO_3 served as the hole- and electron-injecting layers, m-MTDATA and BPhen served as hole- and electron-transporting layers (HTL and ETL), [Ir-(ppz)₃] was used as a hole-transporting and exciton/electronblocking material, and FIrpic was the blue-light-emitting phosphor, respectively. Devices BA-BE were based on DBFSPOPhCz, DBFDPOPhCz, and DBFDPOPhCz₂, as well as conventional blue phosphorescent hosts 1,3-bis(carbazol-9-yl)benzene (**mCP**) and 4,4',4''-tris(carbazol-9-yl)-triphenylamine (**TCTA**) for comparison, respectively (Scheme 3). All of these devices revealed a pure emission from FIrpic (Figure 7a, inset), which confirmed the efficient energy transfer from the hosts to the phosphor.

Inspiringly, $DBF_rPOPhCz_n$ also endowed their devices (BA-BC) with extremely low driving voltages (2.4 V for onset, about 2.8 V at 200 cd m^{-2} , and < 3.4 V at 1000 cd m^{-2} ; Figure 7 a and the Supporting Information, Table S1), which were the same as those of **DBF**_{*r*}**POC**_{*z*_{*n*}-based devices with} similar configurations.^[9] This result further indicates the limited influence of the π spacer on the carrier-injecting and -transporting abilities of the D- π -A systems. Compared with devices BD and BE, which were based on the conventional mCP and TCTA structures, the driving voltages of devices BA-BC were dramatically decreased (by 0.3 V for onset, 0.4 V at 100 cdm^{-2} , and 0.5 V at 1000 cdm^{-2}). Devices BA-BC have very similar driving voltages at a luminance of less than 1000 cdm^{-2} , which is in accord with the closer FMO energy levels of $DBF_xPOPhCz_n$. Nevertheless, the J value of **BA** was much higher than those of **BB** and **BC** at the same voltage. Although the hole-transporting ability of **DBFSPOPhCz** is the weakest, because the minor carrier in the prototype devices is electrons as the bottleneck of current increases, the much stronger electron-transporting ability of **DBFSPOPhCz** gives rise to the remarkable enlarged current in device BA. However, the luminance of devices **BB** and **BC** was equivalent to—and even slightly higher than-that of BA at voltages below 3.5 V, which should be attributed to the relatively balanced carrier injection and transportation in devices BB and BC. On the contrary, at higher voltages, along with the rapid increase of exciton concentration, the luminance of devices BB and BC became lower than that of **BA**. This result reflects the weaker triplet exciton stability of **DBFDPOPhCz**_n, owing to their larger



Figure 7. Brightness-current-density (J)-voltage curves (a), EL spectra (inset), and efficiency-brightness curves (b) of blue-light-emitting PHO-LEDs based on **DBF**_x**POPhC**_{z_n}.

conjugation and poorer structural rigidity, as shown in the optical analysis.

When we designed these $D-\pi$ -A-type hosts, we expected that their higher T_1 levels could further improve the EL efficiencies of their blue-light-emitting PHOLEDs. Although the unbalanced carrier transportation in device BA remarkably decreased its efficiency, its maximum current efficiency (C.E.) was 12.8 cd A^{-1} at 183 cd m^{-2} , which corresponded to a maximum external quantum efficiency (E.Q.E.) of 6.4%; these values were slightly higher than those of device BE but lower than those of device BD (Figure 7b and the Supporting Information, Table S1). Owing to the much lower driving voltages of device BA, its maximum power efficiency (P.E.) was 14.3 Lm W⁻¹, which was equivalent to that of device BD. More significantly, with its much better carriertransporting performance, **DBFDPOPhCz**_n dramatically increased the efficiencies of their devices. The maximum C.E. of devices **BB** and **BC** were 26.7 and 26.1 $cd A^{-1}$ at 60 and 261 cd m⁻², which corresponded to maximum E.Q.E. values of 13.2 and 12.6%, respectively; these values were about 60% higher than those of device **BD** and twice of those of device BE. Owing to the extremely low driving voltages, the maximum P.E. of devices **BB** and **BC** were greatly improved to 30.0 and 31.3 Lm W^{-1} at 60 and 85 cd m⁻², respectively, which were two times that of device BD and three times

that of device **BE**. At 200 cdm^{-2} (for displays), the C.E. values of devices BB and BC decreased to 26.2 and 26.1 cd A^{-1} , which corresponded to E.Q.E. values of 13.0 and 12.6%, respectively, with a roll-off of less than 2%. Their P.E. values also decreased to 27.4 and 29.3 Lm W^{-1} , with a roll-off of 9 and 6%, respectively. At 1000 cdm^{-2} (for indoor lighting), their efficiencies were further decreased to 22.8 and 23.1 cd A^{-1} , 19.9 and 21.3 Lm W^{-1} , and 11.3 and 11.1%, which corresponded to roll-off values of 15 and 11% for C.E., 34 and 32% for P.E., and 14 and 12% for E.Q.E., respectively. Notably, along with the increase in brightness, the decrease in efficiency of devices **BB** and **BC** was remarkably larger than that of devices BD and BE. The unstable triplet excited states mainly originated from the extended conjugation and lower molecular rigidity of **DBFDPOPhCz**_n. Nevertheless, the efficiencies of devices **BB** and **BC** were still much higher than those of devices **BD** and **BE** at a luminance of less than 5000 cdm⁻². Furthermore, compared with **DBFDPOCz**_n-based devices, the maximum efficiencies of devices BB and BC were elevated by at less 20%. However, the efficiency stability of devices BB and **BC** was inferior. This result further indicates that $D-\pi$ -A systems with higher T_1 levels can lead to a remarkable increase in maximum EL efficiency, through suppressing the CT effect, at a cost of weakening the excited-state stability owing to the extension of conjugation and the decrease of molecular rigidity. Nevertheless, because at practical luminance levels, **DBFDPOPhCz**, supported their blue-lightemitting PHOLEDs with much higher efficiencies without sacrificing driving voltages, devices **BB** and **BC** are among the most efficient low-voltage-driven blue-light-emitting PHOLEDs reported so far.

Furthermore, we also fabricated green-, yellow-, and redlight-emitting PHOLEDs based on **DBFxPOPhCz**_n, namely GA-GC, YA-YC, and RA-RC, respectively. The device configurations were similar, except for the phosphors ([tris(2-phenylpyridine)iridium] ([Ir(ppy)₃]) for green-lightemitting devices, [bis(2-phenyl-6-fluorobenzothiozolato)iridium(acetylacetonate)] ([Ir(F-bt)2acac]) for yellow-lightemitting devices, and [bis(2-methyldibenzo-[f,h]quinoxaline)iridium(acetylacetonate)] ([Ir(MDQ)₂acac)] for red-light-emitting devices) and the doping concentration (6 wt. %; Scheme 3). The efficient host-guest energy transfer was demonstrated by the pure emissions from the dopants in the EL spectra. All of the devices revealed improved I-Vcharacteristics. The driving voltages of devices GA-GC were also as low as about 2.4 V for onset, about 2.8 V at 200 cd m⁻², and < 3.4 V at 1000 cd m⁻², which were similar to those of devices **YA-YC** (Figure 8a, c, e and the Supporting Information, Table S1). Devices **RA-RC** had the higher driving voltages (2.8 V for onset, 3.6-4.6 V at 200 cd m⁻²). The I-V characteristics of these devices were almost the same as those of devices BA-BC. The strongest electrontransporting ability of DBFSPOPhCz supported the highest J values of devices GA, YA, and RA. For green- and vellow-light-emitting devices, at high voltages, the luminance of **DBFDPOPhCz**_n-based devices was less than those based



Figure 8. Brightness-current-density-voltage curves (a, c, e), EL spectra (insets), and efficiency-brightness curves (b, d, f) of green- (a, b), yellow- (c, d), and red-light-emitting PHOLEDs (e, f) based on $DBF_xPOPhCz_n$.

on **DBFSPOPhCz**. Owing to the much bigger excited energy gap for energy transfer to red dopants, the unstable excitons of **DBFDPOPhCz**_n became much easier to quench. Therefore, the luminance of devices **RB** and **RC** was remarkably lower than that of device **RA**. On the other hand, $[Ir(ppy)_3]$, $[Ir(F-bt)_2acac]$, and $[Ir(MDQ)_2acac]$ can facilitate the hole injection and transportation, which can modify the unbalanced carrier-injecting/transporting in **DBFSPOPhCz**. Therefore, devices **GA** and **YA** showed comparable efficiencies to those of **GB**, **YA**, and **YB**, respectively. Furthermore, with the advantage of **DBFSPOPhCz** in terms of exciton stability, the efficiency of device **RA** was much higher than those of devices **RB** and **RC**.

The EL performance of these devices reflects the fact that the higher T_1 state in these D– π –A-type hosts is beneficial for their EL efficiencies. In addition, the π spacers hardly influence their *I–V* characteristics. Therefore, the efficiencies of these devices can be remarkably improved with the pres-

ervation of ultralow driving voltages as a feature of ambipolar hosts, even though the extended conjugation and lower molecular rigidity of $D-\pi-A$ system also weaken their efficiency stability.

Conclusion

In conclusion, a series of D- π -A-type phosphine-oxide hosts $(\mathbf{DBF}_{\mathbf{x}}\mathbf{POPhCz}_{n})$ with phenylcarbazole, \mathbf{DBF} , and DPPO moieties to afford high T₁ and ambipolar characteristics were designed and synthesized. The incorporation of phenyl groups as π spacers increased the structural adjustability of these molecules and resulted in improved thermal and morphological stability. Photophysical analysis showed that the S₁ states of **DBF**, **POPhCz**, could be feasibly tuned through adjusting the number and ratio of functional groups. Significantly, phenyl π spacers effectively weakened the CT between the carbazolyl and DBF moieties. Therefore, the influence of CT on the excited states was restrainwith their D-A-type ed. Compared analogues $(\mathbf{DBF}_{x}\mathbf{POCz}_{n})$, the T_{1} states of $\mathbf{DBF}_{x}\mathbf{POPhCz}_{n}$ (about 3.0 eV) are successfully elevated by about 0.1 eV. Furthermore, DFT calculations indicate that phenyl π spacers can block the extension of the T₁ excited state, such that the T₁ states are fully localized on either the DBF or carbazolyl groups. Indeed, both DFT calculations and CV analysis demonstrated the ambipolar characteristics of $\mathbf{DBF}_{x}\mathbf{POPhCz}_{n}$ for double-carrier injection. The *I*-V characteristics of single-carrier-only devices that were based on **DBF**_x**POPhC**_{z_n} further confirmed their double-carrier-transporting ability. Although CT is suppressed by the π spacer, the FMO energy levels and carrier-transporting performance of $DBF_xPOPhCz_n$ are close to those of DBF_xPOCz_n . Therefore, through inserting phenyl π spacers, higher T₁ states are achieved without any negative influence on their ambipolar characteristics. The FIrpic-based devices of $DBF_xPOPhCz_n$ had ultralow driving voltages (2.4 V for onset, <3.4 V at 1000 $\operatorname{cd} m^{-2}$), which were similar with those for devices that were based on DBF_xPOCz_n . Simultaneously, the elevation of the T_1 states of **DBF**_x**POPhC** z_n further increased their efficiency by at least 20% compared with those of **DBF**_{*x*}**POC***z*_{*n*}. Thus, on the basis of $D-\pi$ -A-type **DBF**_x**POPhCz**_n, highly efficient ultralow-voltage-driven blue-light-emitting PHOLEDs were realized. The performance of the $DBF_xPOPhCz_n$ devices also showed their potential for applications as universal hosts for portable full-color PHOLEDs. Nevertheless, we also noted that these $D-\pi-A$ systems suffered from the lower stability of their excited states, owing to their extended conjugation and lower structural rigidity, which worsened the decrease in efficiency at high brightness and J values. To solve this problem, moreaccurate configuration control, on the basis of rational mixed linkages, is imperative and work towards this goal is underway in our laboratory.

Experimental Section

Materials and instrumentation: All reagents and solvents for the synthesis of the title compound were purchased from Aldrich or Acros and used without further purification. (2-Bromo)-(4-diphenylphosphoryl)dibenzofuran (**DBFSPOBr**), (8-bromo)-(4,6-bis(diphenylphosphoryl)) dibenzofuran (**DBFDPOBr**), and (2,8-dibromo)-(4,6-bis(diphenylphosphoryl))dibenzofuran (**DBFDPOBr**₂) were prepared according to our previous report.^[9]

¹H NMR spectroscopy was performed on a Varian Mercury plus 400NB spectrometer relative to tetramethylsilane (TMS) as an internal standard. Molecular mass was determined on a FINNIGAN LCQ mass spectrometer (ESI) or on a MALDI-TOF MS. Elemental analysis was performed on a Vario ELIII elemental analyzer. Absorption and PL emission spectra of the target compound were measured on Shimadzu UV-3150 and RF-5301PC spectrophotometers, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Shimadzu DSC-60A and DTG-60A thermal analyzers under a nitrogen atmosphere at a heating rate of 10°C min⁻¹. Cyclic voltammetry (CV) studies were conducted on an Eco Chemie B. V. AUTOLAB potentiostat in a typical three-electrode cell with a platinum-sheet working electrode, a platinum-wire counter electrode, and a silver/silver-nitrate (Ag/Ag⁺) reference electrode. All electrochemical experiments were performed under a nitrogen atmosphere at RT in CH2Cl2. Phosphorescence spectra were measured in CH₂Cl₂ on an Edinburgh FPLS 920 fluorescence spectrophotometer at 77 K under cooling with liquid nitrogen and a delay of 300 µs by using the time-correlated single-photon-counting (TCSPC) method with a microsecond pulsed xenon light source for lifetime measurements in the range 10 µs-10 s; the synchronization photomultiplier for signal collection and the multichannel scaling mode of the PCS900 fast counter PC plug-in card were used for data processing. The thin films of the PO compounds were prepared through vacuum evaporation onto glass substrates under the same conditions for device fabrication. The morphological characteristics of these films were measured by atomic force microscopy (AFM) on an Agilent 5100 under the tapping mode and by SEM on a HITACHI S-4800 (spraying, accelerating voltage: 5.0 kV, current: 10 mA, observed altitude: 8 mm).

Synthesis

(2-(4-(9H-Carbazol-9-yl)phenyl))-(6-diphenylphosphoryl)dibenzofuran (**DBFSPOPhCz**): A 2M aqueous solution of NaOH (3 mL, 6 mmol) was added to a stirring solution of **DBFSPOBr** (447 mg, 1 mmol), 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole

(553 mg, 1.5 mmol), $[Pd(PPh_3)_4]$ (116 mg, 0.1 mmol), and tetra-*n*-butylammonium bromide (TBAB, 32 mg, 0.1 mmol) in THF (10 mL). Then, the reaction mixture was warmed to 90 °C and stirred for 24 h. The reaction was quenched with an aqueous solution of NH₄Cl (10 mL) and extracted with CH₂Cl₂ (3×10 mL). The organic layer was dried with anhydride Na₂SO₄. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1–0:1) to obtain the product as a white powder (415 mg, 68 % yield).

¹H NMR (TMS, CDCl₃, 400 MHz): δ =8.258 (d, *J*=7.6 Hz, 2H), 8.188 (d, *J*=7.6 Hz, 2H), 7.927–7.826 (m, 7H), 7.760 (dd, *J*=8.6, 1.8 Hz, 1H), 7.694 (d, *J*=8.4 Hz, 2H), 7.640–7.436 (m, 12H), 7.338 ppm (t, *J*=7.4 Hz, 2H); MS (LDI-TOF): *m/z* (%): 610 (100) [*M*]⁺; elemental analysis calcd (%) for C₄₂H₂₈NO₂P: C 82.74, H 4.63, N 2.30, O 5.25; found: C 82.91, H 4.65, N 2.42, O 5.51.

(2-(4-(9H-Carbazol-9-yl)phenyl))-(4,6-bis(diphenylphosphoryl))dibenzofuran (**DBFDPOPhCz**): A 2M aqueous solution of NaOH (3 mL, 6 mmol) was added to a stirring solution of **DBFDPOBr** (647 mg, 1 mmol), 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9Hcarbazole (553 mg, 1.5 mmol), [Pd(PPh_3)_4] (116 mg, 0.1 mmol), and TBAB (32 mg, 0.1 mmol) in THF (10 mL). Then, the reaction mixture was warmed to 90 °C and stirred for 24 h. The reaction was quenched with an aqueous solution of NH₄Cl (10 mL) and extracted with CH₂Cl₂ (3×10 mL). The organic layer was dried with anhydride Na₂SO₄. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1–0:1) to obtain the product as a white powder (470 mg, 58 % yield).

¹H NMR (TMS, CDCl₃, 400 MHz): δ =8.485 (t, *J*=1.6 Hz , 1H), 8.321 (q, *J*=13.6, 2.0 Hz, 1H), 8.271 (d, *J*=7.6 Hz, 1H), 8.175 (d, *J*=7.6 Hz, 2H), 7.882 (d, *J*=8.4 Hz, 2H), 7.809–7.607 (m, 11H), 7.548–7.446 (m, 9H), 7.445–7.359 (m, 8H), 7.360–7.300 ppm (m, 2H); MS (LDI-TOF): *m*/*z* (%): 810 (100) [*M*]⁺; elemental analysis calcd (%) for C₅₄H₃₇NO₃P₂: C 80.09, H 4.61, N 1.73, O 5.93; found: C 80.14, H 4.67, N 1.86, O 6.14.

(2,8-Bis(4-(9H-carbazol-9-yl)phenyl))-(4,6-bis(diphenylphosphoryl))dibenzofuran (**DBFDPOPhCz**₂): A 2M aqueous solution of NaOH (6 mL, 12 mmol) was added to a stirring solution of **DBFDPOBr**₂ (726 mg, 1 mmol), 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9Hcarbazole (1106 mg, 3 mmol), [Pd(PPh₃)₄] (232 mg, 0.2 mmol), and TBAB (64 mg, 0.2 mmol) in THF (20 mL). Then, the reaction mixture was warmed to 90 °C and stirred for 24 h. The reaction was quenched with an aqueous solution of NH₄Cl (10 mL) and extracted with CH₂Cl₂ (3× 10 mL). The organic layer was dried with anhydride Na₂SO₄. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1–0:1) to obtain the product as a white powder (610 mg, 58% yield).

1H NMR (TMS, CDCl₃, 400 MHz): δ =8.584 (s, 2H), 8.232 (q, *J*=13.4, 1.8 Hz, 2H), 8.176 (d, *J*=7.6 Hz, 4H), 7.879 (d, *J*=8.4 Hz, 4H), 7.801–7.670 (m, 12H), 7.573–7.386 (m, 20H), 7.371–7.298 ppm (m, 4H); MS (LDI-TOF): *m/z* (%): 1051 (100) [*M*]⁺; elemental analysis calcd (%) for C₇₂H₄₈N₂O₃P₂: C 82.27, H 4.60, N 2.67, O 4.57; found: C 82.35, H 4.62, N 2.79, O 4.65.

Theoretical calculations: DFT computations were carried out with different parameters for structure optimization and vibration analysis. The ground states and triplet states of the molecules in vacuo were optimized without any assistance of experimental data by using the restricted and unrestricted formalism of Beck's three-parameter hybrid-exchange functional^[20] and the Lee, Yang, and Parr correlation functional,^[21] that is, (B3LYP)/6–31G(d), respectively. The fully optimized stationary points were further characterized by harmonic vibrational frequency analysis to ensure that "real" local minima had been found without any imaginary vibrational frequencies. The total energies were also corrected by zeropoint energies, both for the ground states and the triplet states. The spindensity distributions were visualized with Gaussview 3.0. All computations were performed by using the Gaussian 03 package.^[22]

Device fabrication: Prior to the device fabrication, the patterned ITOcoated glass substrates were scrubbed and sonicated successively with acetone, EtOH, and deionized water. All of the organic layers were thermally deposited under vacuum (about 4.0×10^{-4} Pa) at a rate of 1-2 Ås⁻¹ and monitored in situ by the quartz oscillator. To reduce the ohmic loss, a heavily *p*-doped layer with MoO_x, considering the low doping efficiency into an amorphous organic matrix with transition-metal-oxide-based acceptors, was directly deposited onto the ITO substrate for each sample. After the deposition of LiF, the samples were transferred into a metal chamber and suffered from a vacuum break owing to the change of the shadow masks to determine the active area. Their current–voltage–luminance characteristics were measured on a PR650 spectrascan spectrumeter with a Keithley 2400 programmable voltage–current source. All of the samples were measured directly after fabrication without encapsulation under ambient conditions.

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1396 -