Excited-State Tuning

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Controllably Tuning Excited-State Energy in Ternary Hosts for Ultralow-Voltage-Driven Blue Electrophosphorescence**

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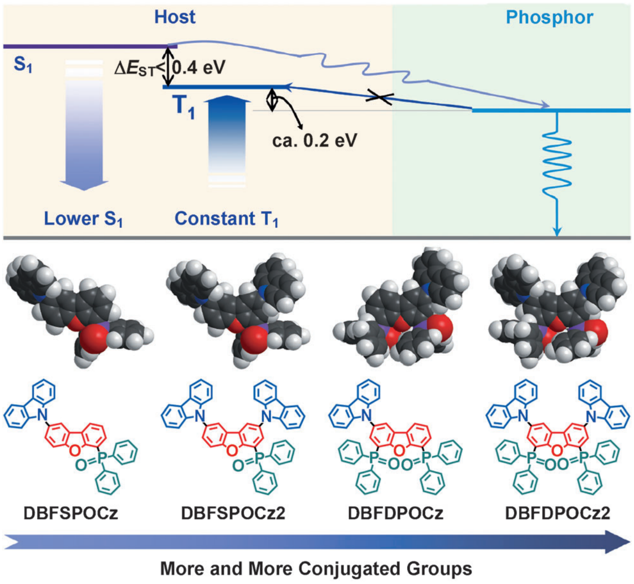
Phosphorescent organic light-emitting diodes (PHOLEDs), with 100% theoretical internal efficiency, are being rapidly developed as a most promising approach to meet the urgent and extensive demand of energy-efficient and portable digital terminals and lighting sources.[1] Thanks to the recent breakthrough of highly efficient blue PHOLEDs[2] and outcoupling technologies, PHOLEDs in full color can already realize extremely high efficiencies that approach those of fluorescent tubes (about 70 Lm W^{-1}).[3] Nevertheless, as the hosts in the emitting layers (EMLs) should have higher triplet excited energy levels (T_1) to confine the excitons on phosphorescent guests,[4] the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gaps in PHOLEDs are often much larger than their fluorescent counterparts, which consequently result in poor energy-level alignment and thus higher driving voltages. This drawback not only complicates the design of driving circuit, but also directly reduces power efficiency (PE).[5] Thus, the low-voltage-driving high-efficiency PHOLED remains the biggest challenge. Su, Kido, et al. have reported green PHOLEDs with extremely low operating voltages of 2.18 V for onset and 2.41 V at 100 cd m^{-2} through good management of the interfacial contact between electron transporting layers and anodes.[5] However, there are only a few blue PHOLEDs that achieve low driving voltages; for example, applicable luminance at a driving voltage of less than 3 V.[6] The formidable challenge is the high barriers for carrier injection and transportation deriving from the prerequisite of extremely high T_1 of the hosts, for example, 2.85 eV (0.2 eV higher than that of blue phosphor iridium(III)bis(4,6-(difluorophenyl)pyridinato-N,C2)picolinate (FIrpic; Scheme 1). This issue actually reflects the intrinsic contradiction between optical and electrical properties of the materials. As the singlet excited energy levels (S_1) are related to HOMO–LUMO energy gaps, the challenge has actually evolved into an original scientific problem: how to controllably adjust S_1 without changing T_1. Unfortunately, as most of the modification approaches have the same effects on both singlet and triplet states,[7] only few hosts possess both of the energy difference between S_1 and T_1 (ΔE_{ST}) of less than 0.4 eV and T_1 of more than 2.85 eV.[6b]



Scheme 1. The energy-transfer process in phosphorescent doping systems, and molecular structures of DBF*x*POCz*n*.

We recently reported several ambipolar ternary aryl phosphine oxide (APO) hosts based on indirect linkage.[6b] Their ΔE_{ST} was tuned to 0.45 eV, and low driving voltages and high efficiencies were realized. However, the indirect linkage can hardly afford multiple modifications. We believe that the

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development of ternary systems composed of chromophores and hole and electron transporting moieties on the basis of reasonable linkages should be one of the most promising pathways to achieve high energy-gap hosts with improved carrier injecting/transporting ability,[8] because 1) high T_1 hole and electron injecting can be contributed by the relative groups; 2) more complicated molecular structures can be established to finely tune the optoelectronic properties; and 3) the carrier injecting/transporting can be accurately modulated through varying the number and ratio of the carrier transporting moieties so as to find the ideal molecular structures.

Herein, we present an effective strategy for constructing ambipolar hosts with high T_1 through the mixed *meso*- and short-axis linkages, which is proved by four ternary hosts based on dibenzofuran (DBF) as chromophore, which mainly determines the optical characteristics, hole-transporting carbazolyl, and electron-transporting diphenylphosphine oxide (DPPO), namely 2-carbazolyl-6-(diphenylphosphinoyl)dibenzofuran (DBFSPOCz), 2,8-dicarbazolyl-4-(diphenylphosphinoyl)dibenzofuran (DBFSPOCz2), 2-carbazolyl-4,6-bis-(diphenylphosphinoyl)dibenzofuran (DBFDPOCz), and 2,8-dicarbazolyl-4,6-bis-(diphenylphosphinoyl)dibenzofuran (DBFDPOCz2; Scheme 1 and Supporting Information, Scheme S1). They are collectively named DBF*x*POCz*n*. Upon their gradually increased π-conjugation by changing the number and ratio of carbazolyl and DPPO from 1:1, 2:1, and 1:2 to 2:2, we successfully reduced S_1 values whilst simultaneously maintaining T_1 values of these hosts at around 2.90 eV. DBFDPOCz supported FIrpic-based PHOLEDs with the extremely low driving voltages, such as 2.4 V for onset, which is even 0.25 V lower than that corresponding to the photon energy (2.65 V, *hν*/e). The luminance of 100 cd m^{-2} for display and 1000 cd m^{-2} for indoor lighting were also achieved at <2.8 V and <3.3 V. To the best of our knowledge, these data are the lowest among the prototype blue PHOLEDs without additional enhancing technology. This work suggests a brand new concept to construct high energy-gap hosts with mixed linkages and shows the huge potential of ternary hosts in highly efficient blue PHOLEDs for portable applications.

In DBF*x*POCz*n*, carbazolyl moieties are introduced at 2,8-positions of DBF, while DPPOs bond to DBF along molecular short axis. Carbazolyl moieties and DPPOs are at *meta* position to each other so as to suppress the interplay between them. The decomposition temperature at a weight loss of 5% (T_d) from DBFSPOCz to DBFDPOCz2 increased remarkably owing to the reduced molecular volatility and increasing π-conjugation (Supporting Information, Figure S1 and Table S1). The rigid molecular configurations of DBF*x*POCz*n* endow them with high glass-transition temperatures (T_g) of over 100 °C. The good morphological properties were further indicated through AFM (Supporting Information, Figure S2) and SEM images (Supporting Information, Figure S3) of the vacuum-evaporated thin films. No aggregation and crystallization were observed. The root-mean-square roughness (RMS) of 0.24–0.94 nm testifies the excellent film-forming ability of these compounds. More carbazolyl moieties or DPPOs slightly increase the roughness, which is ascribed to the less controllable deposition for bigger molecules under same evaporation condition.

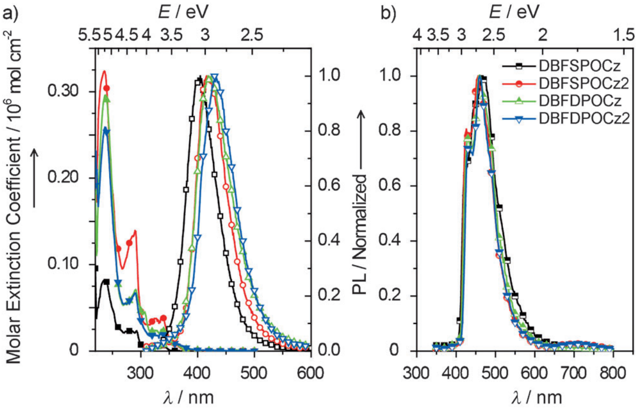

Figure 1. a) UV/Vis absorption spectra and fluorescence spectra of DBF*x*POCz*n* in dilute dichloromethane (10^{-6} mol L^{-1}); b) Phosphorescence spectra of DBF*x*POCz*n* in dichloromethane at low temperature (77 K) after a delay of 300 μs to eliminate fluorescence.

The UV/Vis spectra of DBF*x*POCz*n* include three main absorption bands in the ranges of 200–250, 250–300 and 300–375 nm, corresponding to the $\pi \rightarrow \pi^*$ transitions of phenyl in DPPOs, DBF, and the mixed transitions of limited charge-transfer (CT) states and $\pi \rightarrow \pi^*$ transitions from carbazolyl to DBF moieties, respectively (Figure 1 a; Supporting Information, Figure S4). The molar extinction coefficients of DBFDPO derivatives are much smaller than DBFSPOCz2. Furthermore, DBFDPOCz2, with the biggest hindrance, showed a slightly lower extinction coefficient than that of DBFDPOCz. The excitation spectra also exhibit the same situation (Supporting Information, Figure S5). The main reason might be that the much enhanced steric hindrance by doubled DPPOs in DBFDPOCz and DBFDPOCz2 restrains their configuration adjustment in excited states. Nevertheless, it is not surprising that the optical energy gaps are remarkably reduced from 3.52 to 3.26 eV, along with the increase of π-conjugation (Table 1). The variation tendency of the fluorescent emissions of DBF*x*POCz*n* is the same. A more careful comparison reveals that the second carbazolyl group results in the reduction of energy gap for 0.1 eV, while the second DPPO seems more effective with the reduction of 0.15 eV. This is much different in binary systems (such as carbazole-DPPO hybrids[9]), in which DPPO moieties nearly do not change the energy gaps. In films, the absorption spectra of DBF*x*POCz*n* still retain the corresponding fine structures (Supporting Information, Figure S6 and Table S1). The shift of their solid-state emissions can also be negligible. It further implies limited intermolecular interaction and aggregation. More significantly, it is inspiring that the phosphorescence spectra of DBF*x*POCz*n* are perfectly fixed in shape and range (Figure 1 b; Supporting Information, Figure S7). All of these compounds have high T_1 of about 2.90 eV for efficient exothermic energy transfer to FIrpic. T_1 of 2,8-di(carbazol-9-yl)dibenzofuran (*m*-CzOF)[10] was reported as 2.97 eV;

Table 1: Physical properties and device performance of DBF*x*POCz*n*.

Compound	E_g [eV]	T_1 [eV]	Voltage [V][c]	Efficiency roll-off [%][d]
DBFSPOCz	3.52[a] 3.91[b]	2.90[a] 2.98[b]	2.5, <3.0, <3.6	27, 45, 27
DBFSPOCz2	3.42[a] 3.78[b]	2.91[a] 2.85[b]	2.4, <2.8, <3.5	10, 26, 14
DBFDPOCz	3.37[a] 3.67[b]	2.88[a] 2.82[b]	2.4, <2.8, <3.3	7, 15, 7
DBFDPOCz2	3.26[a] 3.51[b]	2.88[a] 2.76[b]	2.4, <2.8, <3.5	15, 31, 16

[a] Calculated by the absorption edges. [b] DFT calculation results. [c] In the order of onset, 100, and 1000 cd m^{-2}. [d] In the order of CE [cd A^{-1}], PE [lm W^{-1}], and EQE [%] at 1000 cd m^{-2}.

therefore, the incorporation of DPPO has the slight influence of about 0.07 eV on T_1. Furthermore, the introduction of another DPPO along short axis can only induce the reduction of T_1 for 0.02 eV, and T_1 cannot be changed by the second carbazolyl group. DFT calculations of their T_1 states showed a similar tendency (Table 1). Actually, the spin-density distributions of T_1 states indicate that although T_1 state of DBFSPOCz is determined by the carbazolyl group, DBF in the other three molecules has the dominant influence on their T_1 states (Supporting Information, Figure S8). As the interactions between DPPO and carbazolyl are blocked by DBF and *meso* linkage, the only intramolecular interplay is the weak charge transfer between carbazolyl and DBF, which is shown by the stable PL emissions of DBF*x*POCz*n* in solvents with various polarities and the similar bathochromic interval less than 20 nm with that of 2,8-di(carbazol-9-yl)dibenzofuran (DBFCz2; Supporting Information, Figure S9). Therefore, in these ternary systems, all of the building blocks have been well-managed to maintain T_1 to the greatest extent. The ΔE_{ST} value is consequently reduced from 0.62 to 0.38 eV. Thus, it is feasible to fix T_1 and simultaneously tune S_1 on the basis of the reasonable combination of molecular composition and linkage modes.

DFT calculation further presents the same tendency for the energy gaps to decrease along with the increase of π-conjugation (Figure 2). The HOMO and LUMO+1 of these molecules are located on their carbazolyl and DPPO groups, respectively, while LUMOs are mainly contributed by DBF. Therefore, through introducing carbazolyl and DPPO groups, the carrier injection ability is effectively improved. Notably, more functional groups increase the frontier molecular orbital (FMO) density by inserting new MOs into the interspaces without remarkably influencing the original MO distributions. Thus, in ternary systems, the influence of electron-donating groups and electron-withdrawing groups on energy gaps can be combined rather than neutralized by suitable linkages. HOMOs of DBF*x*POCz*n* are similar about −6.1 eV, as determined by cyclic voltammetry (Supporting Information, Figure S10 and Table S1). However, DBFDPOCz and DBFDPOCz2 have lower LUMOs. This implies that the number of DPPO groups and electron-injecting ability are proportional. The nominal single-carrier transporting devices based on DBF*x*POCz*n* and DBFCz2 were also fabricated to investigate their carrier transporting abilities (Supporting Information, Figure S11). Compared with the monocarbazolyl derivatives, DBFSPOCz2 and DBFDPOCz2 have the more balanced carrier transporting ability owing to their enhanced hole-only current densities (*J*) and reduced electron-only *J*. This is attributed to the embedding and blocking of DBF by more peripheral carbazolyl moieties. Actually, DBF can also make considerable contributions to electron transportation. Therefore, DBFSPOCz with the least substituents and DBFDPOCz2 with the symmetrical configuration have the stronger electron transporting ability than DBFDPOCz and DBFSPOCz2, respectively. Simultaneously, the hole transporting abilities of DBFSPOCz2 and DBFDPOCz2 are comparable to that of DBFCz2, while their electron transporting abilities are much stronger. This further indicates the suppressed interference between carbazolyl moieties and DPPOs owing to the rational linkages. In general, we can readily control the carrier injecting/transporting ability of the molecules through changing the number, ratio, and type of the functional groups and the molecular configurations. The dramatic progress is that it has almost no influence of T_1.

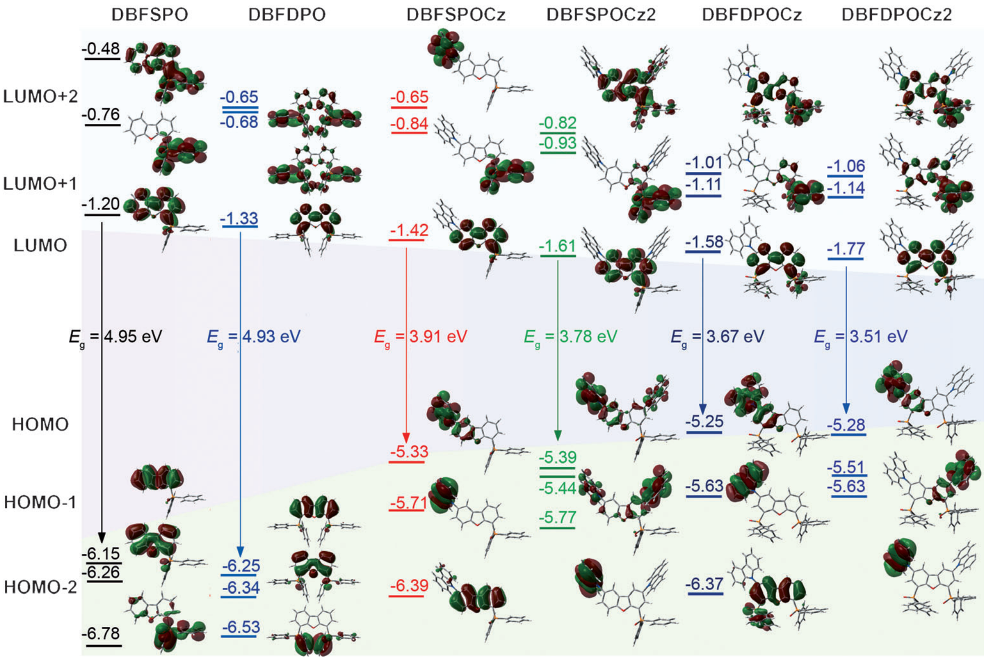

Figure 2. DFT-calculated energy levels of DBFSPO, DBFDPO, and DBF*x*POCz*n*.

The harmonized optoelectronic characteristics of DBF*x*POC*zn* encouraged us to fabricate blue-emitting PHOLEDs based on FIrpic (Supporting Information, Scheme S2). Devices **A**–**D** used DBFSPOCz, DBFSPOCz2, DBFDPOCz, and DBFDPOCz2 as hosts, respectively. For comparison, Devices **E** and **F** were also fabricated with the conventional hosts 1,3-dicarbazolylbenzene (mCP) and tris(4-(9*H*-carbazol-9-yl)phenyl)amine (TCTA). It is inspiring that the turn-on voltages of **B**–**D** were extremely low as 2.4 V, which is even 0.25 V lower than the theoretical threshold voltage corresponding to the emission photon energy of FIrpic (2.65 eV; Figure 3 a and Table 1).[5] This value also approaches the limit of 2.2 V for the ideal blue-emitting OLEDs.[11] DBFDPOCz provided **C** with the ultralow driving voltages, such as < 2.8 V at 100 cd m^{-2} for display and < 3.3 V at 1000 cd m^{-2} for indoor lighting. These data were much lower than those of the devices based on unipolar analogues of DBFDPOCz[10,12] and devices **E** and **F**. To the best of our knowledge, this is the best result for ultralow-voltage-driven blue-emitting PHOLEDs with the conventional structures (Supporting Information, Table S2). Although **A** achieved the highest efficiencies among these devices, its sharp decline of efficiencies at high luminance and *J* implies the unbalanced carrier injection and transportation in its EML. This should be attributed to the much stronger electron transporting ability of DBFSPOCz. **C** also realized the much higher efficiencies compared with **E** and **F**; furthermore, its efficiency roll-off was much reduced. At 1000 cd m^{-2}, its external quantum efficiency decreased for only 7 % of the maximum. It is noteworthy that the EL performance of **B** and **D** was much worse than that of **A** and **C**, although DBFSPOCz2 for **B** and DBFDPOCz2 for **C** have more balanced carrier transporting abilities than those of DBFSPOCz and DBFDPOCz. As in the common devices the current is hole-dominant and Ir^{3+} complexes often have strong trapping ability, the moderately dominant electron transportation in the host may facilitate the charge balance in EMLs. In this case, it is crucial to modulate the carrier transporting ability of the host accurately to fit to the entire conditions of the devices, which is one of the unique advantages of ternary host systems.

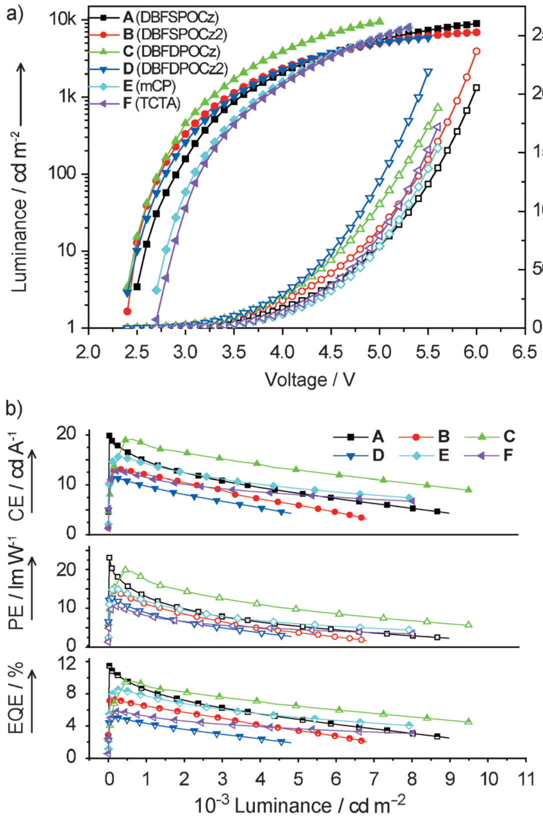

Figure 3. a) Current density *J* versus voltage (hollow symbols) and luminance (solid symbols) versus voltage curves of devices **A**–**F**; b) efficiency–luminance curves of **A**–**F**.

In summary, on the basis of the mixed *meso* and short-axis linkages, we have fixed T_1 and continuously tuned S_1 of DBF-based ternary hosts. The S_1 variation actually corresponds to the accurate modulation of carrier injection and transportation in the host materials. In this sense, we have successfully overcome the intrinsic contradiction between optical and electrical properties, and have consequently constructed the promising hosts with both high T_1 of about 2.90 eV and specific ambipolar characteristics. The efficient blue electrophosphorescence was achieved under the extremely low driving voltages, such as 2.8 V at 100 cd m^{-2} for displays. This proof-of-concept study not only develops an effective method to control molecular excited energy levels, but also presents a novel strategy for construct ambipolar high-energy-gap hosts and the great potential of these ultralow-voltage-driven PHOLEDs for the future applications in pocket digital terminals directly driven by low-voltage sources, such as solar cells.

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