ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Tuning Charge Balance in Solution-Processable Bipolar Triphenylamine-diazafluorene Host Materials for Phosphorescent Devices

Zhaokang Fan,[†] Huiru Zhao,[‡] Nengquan Li,[†] Yiwu Quan,[*,†] Qingmin Chen,[†] Shanghui Ye,[*,§] Shuhua Li,[‡] Ying Wang,[*,#] Quli Fan,[§] and Wei Huang[*,§,⊥]

[†]Department of Polymer Science & Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, [‡]Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

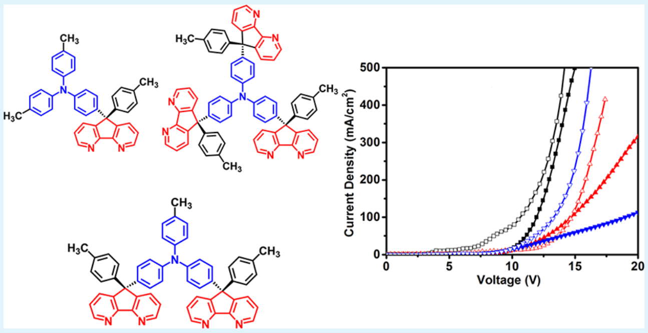
[§]Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials, National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts and Telecommunications, Nanjing 210023, China

[⊥]Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials, National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 211816, China

[#]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Supporting Information

ABSTRACT: Three bipolar hosts, namely TPA-DAF, TPA-DAF$_2$, and TPA-DAF$_3$, comprising an electron-donating triphenylamine (TPA) group and electron-accepting 4,5-diazafluorene (DAF) units are investigated for phosphorescent organic light-emitting diodes (PhOLEDs). Given the non-planar structure of the sp^3-hybridized C9 atom in DAF unit, these molecules have a highly nonplanar configuration, good film-forming property, and high triplet energy (E_T) of 2.88–2.89 eV. Among them, TPA-DAF shows more balanced carrier injecting/transporting ability, suitable highest occupied molecular orbital (MO) energy level and higher current density, and therefore TPA-DAF-based devices exhibit the best performances, having an extremely slight efficiency roll-off with current efficiency of 20.0 cd/A at 973 cd/m^2, 19.5 cd/A at 5586 cd/m^2, and 17.6 cd/A at 9310 cd/m^2 for blue PhOLEDs; 23.5 cd/A at 1059 cd/m^2 and 15.3 cd/A at 8850 cd/m^2 for green PhOLEDs; and 12.2 cd/A at 1526 cd/m^2, 10.5 cd/A at 5995 cd/m^2, and 9.2 cd/A at 8882 cd/m^2 for red PhOLEDs, respectively. The results also provide a direct proof for the influence of charge balance on the device performance.



KEYWORDS: *bipolar host, triphenylamine, 4,5-diazafluorene, phosphorescent diodes*

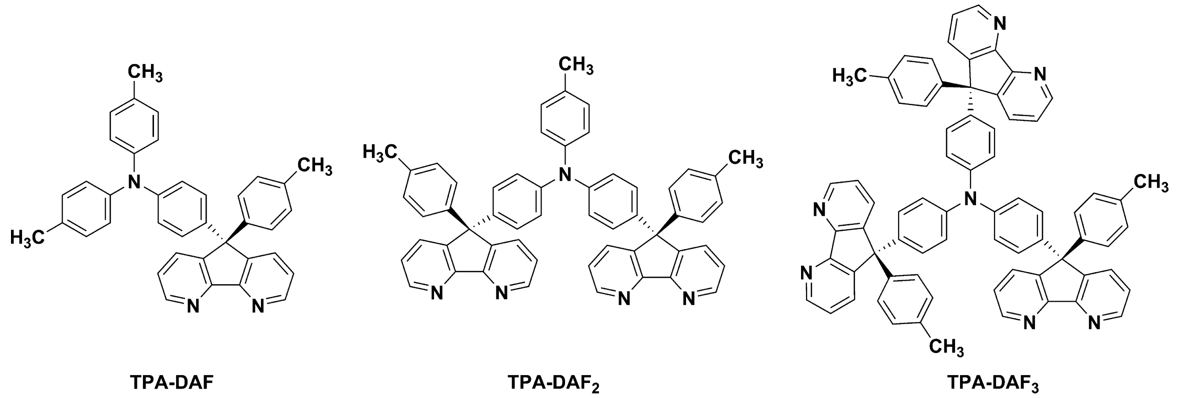
INTRODUCTION

Consisting of an organometallic dopant and a wide band gap host material in the emissive region, phosphorescent organic light-emitting diodes (PhOLEDs) are currently attracting intensive attention because of the effective utility of both singlet and triplet excitons.[1] For the development of efficient PhOLEDs materials, it is essential that the triplet level of the host should be larger than that of the triplet emitter to prevent reverse energy transfer from the emitting dopant back to the host.[2] Such a requirement becomes particularly challenging for the blue PhOLEDs, in which the triplet energy of the host is required to be higher than 2.70 eV.[3] Up to now, because of their wide band gap, high triplet energy, and good charge mobility, triphenylamine (TPA) derivatives,[4−7] as well as carbazole derivatives,[8−15] are most widely explored for host materials. However, the lack of rigidity in twisted TPA molecules may result in the degradation of the thermal and morphological stabilities as host materials in PhOLEDs.[16] Thus far, many efforts have gone into improving the film morphological stability without sacrificing the triplet energy of the TPA host. For example, Shu's group[17] reported the facile synthesis of a fluorene/triarylamine hybrid, tris[4-(9-phenylfluoren-9-yl)phenyl]amine. Ma's group[4,18,19] presented the design of a series of triphenylamine derivatives that were fully or partially bridged with the bulky spacer rigid fluorene and triphenylsilyl units, imparting them high morphological stability. Moreover, the bulky spacer can be electron-transporting groups to balance charge flux and improve the power

Received: December 21, 2014
Accepted: April 21, 2015
Published: April 21, 2015

DOI: 10.1021/am509014v
ACS Appl. Mater. Interfaces 2015, 7, 9445−9452

Scheme 1. Molecular Structures of TPA-DAF, TPA-DAF$_2$, TPA-DAF$_3$



efficiency of devices,[20] such as oxadiazole,[21−24] triazole,[25] phenylphosphine oxide,[26−28] benzofuropyridine,[29,30] tetraarylsilane,[31,32] and 4,5-diazafluorene (DAF).[33−35] These bipolar hosts have advantages arising from more balanced injection and transport of holes and electrons, which results in a broad distribution of recombination region within the emitting layer and a low efficiency roll-off of the devices.

Most of the reported solution-processed PhOLEDs suffered from low efficiency at practical luminance of 1000 cd/m^2 and hence further improvement of charge balance in hosts is needed. However, most of reported bipolar hosts were designed to have a certain ratio of electron-transporting unit to hole-transporting unit, which may impede devices performance as perfect charge balance is hardly achieved. One approache is the use of mixed hosts instead of single host, which has advantage in that charge transporting properties can be freely manipulated by changing the composition of the mixed host.[5,36] But it is difficult to choose hosts for a mixed system because many of them are immiscible, thus leading to phase separation in the film and low efficiency of devices. So an improved method is to design hosts with similar structure but with different charge balance capacity, for example, designing a host with different ratios of hole-transporting moieties to electron-transporting moieties.[37−41]

In our previous work, we proposed a new method to synthesize bipolar hosts with different ratios of electron-transporting (DAF) to hole-transporting units (TPA) through a simple Friedel−Crafts reaction. TPA derivatives reacted with 9-*p*-methylphenyl-4,5-diazafluoren-9-OH (DAFOH, prepared by Grignard reaction previously) in the solution of sulfuric acid:acetic acid (1:100, v/v) to gain TPA-DAF$_n$ (n = 1−3, see Scheme 1) and the structures were fully characterized.[42] For all the prepared bipolar hosts, DAF and TPA units are linked via the sp^3-hybridized C-9 atom in the DAF moiety, thus endowing the molecules with a highly nonplanar configuration and a high E_T. Herein, the influence of the DAF moieties on the electrochemical properties, photophysical behaviors, and EL performances of those bipolar host materials are fully investigated. A direct proof for charge balance's influence on devices performance is demonstrated in this article and the TPA-DAF-based devices show high performances and extremely slight efficiency roll-off at high luminance.

■ EXPERIMENTAL SECTION

Materials and Characterization. TPA-DAF$_n$ (TPA-DAF, TPA-DAF$_2$, TPA-DAF$_3$) are synthesized as in in our previous work.[42] TPBI (1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene), FIrpic [bis(4′,6′-difluorophenylpyridinato) iridium(III) picolinate], Ir(ppy)$_2$(acac) [iridium(III)bis(2-henylpyridinato-N,C2′) acetylacetonate] and Ir(bt)$_2$(acac) [bis(2-phenylbenzothiazolato)(acetylacetonate) iridium(III)] were purchased from a commercial source.

Theoretical calculations on the geometrical and electronic properties were performed with the Gusssian 09 program package.[43] B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals)[44,45] and the 6-31G(d) atomic basis set were used to determine and optimize the structure. Phosphorescence spectrum was measured in 2-MeTHF glass matrix at 77 K. Cyclic voltammetry measurement (CV) was carried on a CHI600 electrochemical analyzer (Chenhua, Shanghai, China) at room temperature with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl standard electrode as reference electrode. The sweep speed was 0.1 V/s. The samples for atomic force microscopy (AFM) test were prepared as the following: First, the ITO-coated glass substrates was spin-coated with PEDOT:PSS, and then solution of TPA-DAF$_n$ doped with 15 wt % FIrpic was spin-coated on it and annealed at temperature of 100 °C for 60 min under nitrogen atmosphere.

Device Fabrication and Characterization. ITO-coated glass substrates were rinsed in deionized water and then ultrasonicated sequentially in acetone and ethanol. Immediately prior to device fabrication, the ITO substrate was treated in a UV-ozone oven for 20 min. Then PEDOT:PSS was spin-coated onto the ITO substrate and dried at 120 °C for 30 min. After that, the emissive layer materials were dissolved in chlorobenzene and spin-coated on the PEDOT:PSS treated substrate. The resulting film was about 35 nm thick, as measured by a Dektak surface profilometer. Finally, TPBI (35 nm) was vacuum-deposited as a hole-blocking layer, and Ca (10 nm) and Ag (100 nm) were deposited as the cathode. The current density, voltage, and luminance characteristics were recorded simultaneously using a computer controlled Keithley 2636A Sourcemeter coupled with Si-photodiodes calibrated with Photo-Research PR-655. The EL spectra were recorded by a PR-655. All the devices were tested in an inert box with no protective encapsulation.

■ RESULTS AND DISCUSSION

Phosphorescence and Theoretical Calculations Properties. Scheme 1 shows the molecular structures of TPA-DAF$_n$. In these molecules, DAF and TPA units are designed to link via the sp^3-hybridized C-9 atom in DAF moiety. These chemical structures were simulated by the density functional theory method (B3LYP) at the 6-311+G(d.p.) level. The optimized conformation with energy minimization shown in Figure 1 suggests that the architecture endows the molecules with a highly nonplanar configuration, which is expected to be capable of suppressing such effects as phase separation and $\pi-\pi$ stacking. In addition, such configuration can effectively limit the extent of conjugation in the hosts and is anticipated to result in

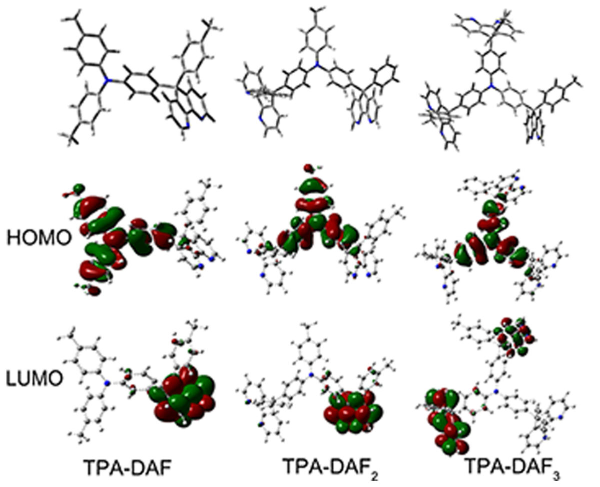


Figure 1. Calculated HOMO and LUMO distribution for TPA-DAF$_n$.

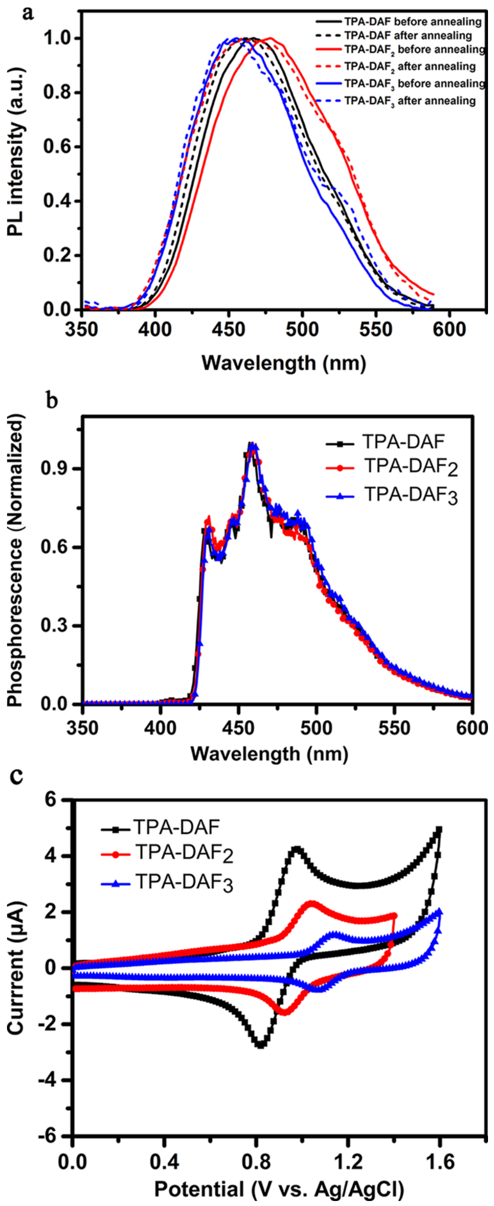


Figure 2. (a) Photoluminescence spectra, (b) phosphorescence spectra, and (c) CV curves of TPA-DAF$_n$.

enhanced E_T and make them potential hosts for blue PhOLEDs. Figure 2a shows the PL spectra of TPA-DAF$_n$ films before and after annealed at 100 °C in a N_2 atmosphere for 2 h. In comparison with TPA-DAF and TPA-$(DAF)_2$, the spectrum of TPA-$(DAF)_3$ blue shifts for about 20 nm which may result from weaker intermolecular interaction due to larger extent of steric hindrance. Moreover, after annealing, all the PL spectra show slight blue-shifts. It can be explained that when molecules are closely packed, the peak is red-shifted, whereas it moves to the blue side when intermolecular distances increase after annealing.[46,47] The phosphorescence (Ph) spectra of three compounds are shown in Figure 2b. Their nearly coincided Ph spectra demonstrated that they had the same E_T and that the number of diazafluorene group introduced to the molecule had little influence on E_T because of the nonconjugated structure. The highest energy vibronic sub-bands of phosphorescent spectra at ~430 nm were used to calculate the E_T and the result showed that they had high enough E_T of 2.88−2.89 eV for blue PhOLEDs. The contributions of carrier transporting groups on TPA-DAF, TPA-DAF$_2$ and TPA-DAF$_3$, were also investigated through the density functional theory (DFT) calculations (Figure 1). As can be expected from the molecular structure, their HOMO and LUMO orbitals are quite localized on the electron-rich triphenylamine and the electron-deficient 4,5-diazafluoren fragments, respectively. It is believed that the separated frontier molecular orbitals can facilitate the balanced carrier injecting/transporting.[12,48] The calculated HOMO and LUMO orbital data are outlined in Table 1.

Electrochemical Properties. The electrochemical properties of TPA-DAF$_n$ were investigated by cyclic voltammetry (CV) using 0.1 M n-Bu_4NPF_6 as the supporting electrolyte and Ag/AgCl as the internal standard (Figure 2c). In the anodic scan in dichloromethane, TPA-DAF, TPA-DAF$_2$, and TPA-DAF$_3$ all exhibited reversible oxidation processes due to their p-type triphenylamine groups, with half-wave potentials of 0.90, 0.98, and 1.10 V respectively, by which the corresponding E_{HOMO} was calculated using the equation of $E_{HOMO} = -(E_{1/2}{}^{OX} + 4.4)$ to be −5.30, −5.38, −5.50 eV. These values together with the photophysical data (absorption onset energy[42]) allowed us to estimate the LUMO energy level to be −1.86, −1.93, and −2.04 eV for TPA-DAF, TPA-DAF$_2$ and TPA-DAF$_3$, respectively. These results, in good agreement with electrochemical test results, reveal that the introduction of DAF groups to the triphenylamine core can lead to the decrease in HOMO and LUMO levels.

Morphology and Charge-Carrier Properties. The film-forming properties of the TPA-DAF$_n$ were also investigated by AFM as they were vital to device performance. As shown in Figure 3, the AFM images of solution-processed TPA-DAF$_n$ films doped with 15 wt % FIrpic annealed at temperature of 100 °C reveal the smooth and homogeneous film morphologies with small values of root-mean-square (RMS) roughness of 0.41 nm for TPA-DAF, 0.40 nm for TPA-DAF$_2$, and 0.69 nm for TPA-DAF$_3$, respectively. This demonstrates that TPA-DAF$_n$ featured by sp^3-hybridized structure has good film-forming property.

To investigate the charge-carrier properties of TPA-DAF$_n$, the hole-only and electron-only devices consisting of the following structures were fabricated respectively (Figure 4): ITO/PEDOT:PSS (15 nm)/TPA-DAF$_n$ (30 nm)/mCP (15 nm)/Ag and ITO/TPBI (15 nm)/hosts (30 nm)/TPBI (15

Table 1. Photophysical Properties of TPA-DAF$_n$ Molecules

host	PH^a (nm)	E_T (eV)	E_{HOMO} (eV)	$E_{LUMO}{}^b$ (eV)	E_g (eV)	$E_{HOMO}{}^c$ (eV)	$E_{LUMO}{}^c$ (eV)	$E_g{}^c$(eV)
TPA-DAF	429	2.89	−5.30	−1.86	3.44	−5.20	−1.73	3.47
TPA-DAF$_2$	430	2.88	−5.38	−1.93	3.45	−5.34	−1.78	3.56
TPA-DAF$_3$	430	2.88	−5.50	−2.04	3.46	−5.47	−1.86	3.61

^{a}Phosphorescence spectrum of hosts in 2-MeTHF at 77 K. ^{b}calculated using equation of LUMO = HOMO + E_g from the photophysical data (absorption onset energy[42]) together with electrochemical data (half-wave oxidation potential). ^{c}According to DFT calculations at B3LYP/6-311+G(d.p.).

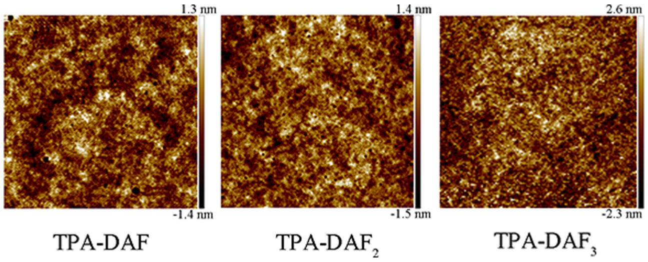


Figure 3. AFM topographic images (5 × 5 μm) of the solution-processed TPA-DAF$_n$ films doped with 15 wt % FIrpic at an annealing temperature of 100 °C for 60 min under a nitrogen atmosphere on the ITO substrate pre-spin-coated with PEDOT:PSS.

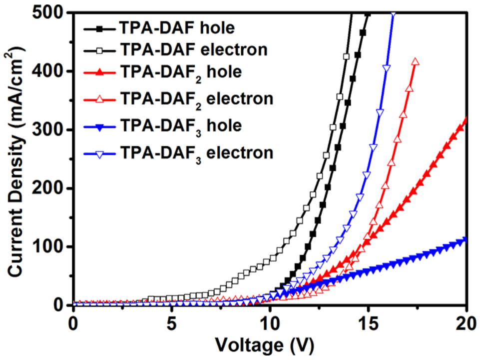


Figure 4. Current density−voltage for the hole-only and electron-only devices of TPA-DAF$_{\mathrm{n}}$.

nm)/Ca (10 nm)/Ag. According to the J−V curves of hole-only devices, the space-charge-limited current (SCLC) hole mobility were calculated to be 1.9×10^{-5}, 4.2×10^{-7}, and 6.3×10^{-7} cm^2/(V s) for TPA-DAF, TPA-DAF$_2$, and TPA-DAF$_3$, respectively. The decrease in the ratio of triphenylamine group contained in the molecule structures leads to a decrease in hole-current densities of DAF, TPA-DAF$_2$, and TPA-DAF$_3$, which can be explained by the higher HOMO energy level and the increased hole mobility of TPA-DAF compared with those of TPA-DAF$_2$ and TPA-DAF$_3$. However, in contrast, the TPA-DAF-based device also shows the highest electron-current density compared to that in the TPA-DAF$_2$ and TPA-DAF$_3$-based devices, with the SCLC electron mobility of 2.5×10^{-5}, 1.2×10^{-6}, and 2.6×10^{-6} cm^2/(V s), respectively. Considering the same physical properties of 4,5-diazafluorene with higher proportions in TPA-DAF$_2$ and TPA-DAF$_3$, the relatively lower electron-transporting properties of these two compounds are probably due to their highly steric configurations, which reduces the solid stacking density of the films, and therefore weakens the electron-transporting capacity. Furthermore, there was a slight difference between the hole- and electron-current densities in the TPA-DAF-based device, proving TPA-DAF could be the best ambipolar host material compared with TPA-DAF$_2$ and TPA-DAF$_3$.

Electroluminescent Properties. In light of the high triplet energies of these bipolar materials, blue electrophosphorescent device B1, B2, and B3 with TPA-DAF, TPA-DAF$_2$, and TPA-DAF$_3$ as a host material was first fabricated, respectively. The device structure was ITO/PEDOT:PSS (25 nm)/host:FIrpic 15 wt % (30 nm)/TPBI (35 nm)/Ca (10 nm)/Ag, where PEDOT:PSS was used as hole-injection layer, and TPBI served as electron-transporting layer. The current density−voltage−luminance (J−V−L) and current efficiency−luminance (CE−L) characteristics are shown in Figure 5. As shown in Figure 5a, in spite of the identical device configuration, the TPA-DAF-

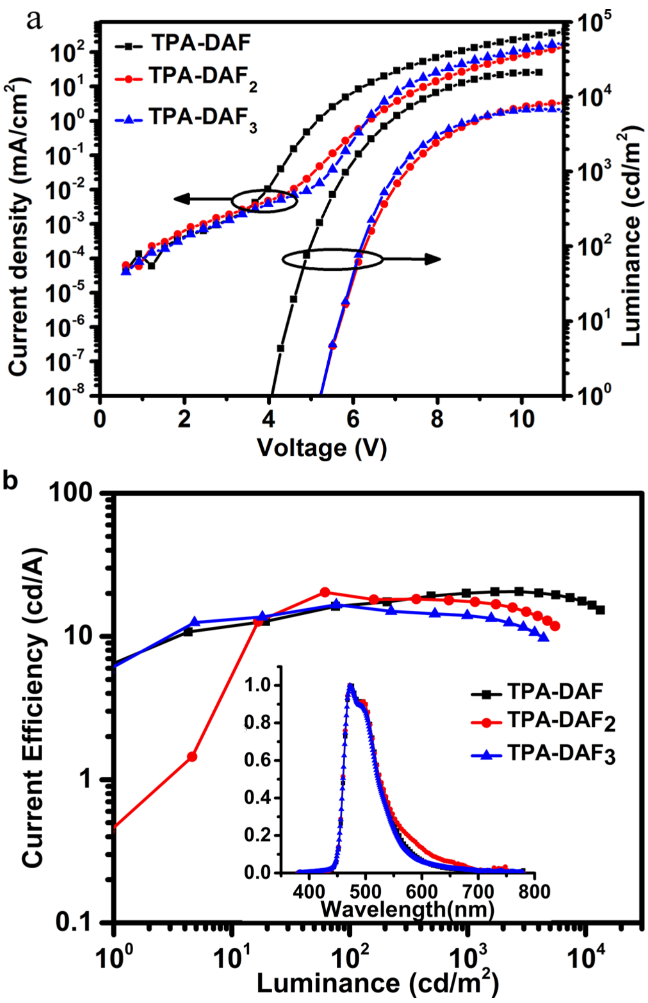


Figure 5. (a) Current density−voltage−luminance; (b) current efficiency−luminance (inset: EL spectrum) with configuration of ITO/PEDOT:PSS (25 nm)/host:FIrpic 15 wt % (30 nm)/TPBI (35 nm)/Ca (10 nm)/Ag(100 nm).

DOI: 10.1021/am509014v
ACS Appl. Mater. Interfaces 2015, 7, 9445−9452

based device exhibited lower turn-on voltage (4.1 V) than TPA-DAF$_2$- or TPA-DAF$_3$-based device (5.3 V). Moreover, in the whole investigated voltage range, the TPA-DAF-based device always delivered higher current density than other devices at a given voltage. The higher current in TPA-DAF-based device should result from the facilitated hole injection and balanced transportation. According to the energy level diagram in Figure 6, the hole injection barrier at the TPA-DAF/PEDOT:PSS interface (0.1 eV) is lower than that at the TPA-DAF$_2$ or TPA-DAF$_3$/TPBI interface (0.18−0.3 eV), which is definitely helpful to enhance hole injection into the emitting layer and result in the lower driving voltages in TPA-DAF-based device. What's more, although the higher LUMO level of TPA-DAF than that of TPA-DAF$_2$ and TPA-DAF$_3$ does not seem to be favorable for electron injection at the TPBI/emitting layer interface, the facilitation of electron injection by the doped low-LUMO-lying FIrpic dominates the electron injection process at the TPBI/emitting layer interface. Therefore, the low-lying LUMO level of FIrpic and the higher-lying HOMO level of TPA-DAF finally result in the lower driving voltage in TPA-DAF-based device. Accordingly, the TPA-DAF-based device exhibited higher brightness with a maximum value of 21134 cd/m^2 at 10.4 V. In contrast, TPA-DAF$_2$- and TPA-DAF$_3$-based devices exhibit maximum luminance of 8348 and 6852 cd/m^2, respectively. TPA-DAF-based device also has a higher maximum external quantum efficiency (EQE) of 8.5%, whereas maximum EQE of the TPA-DAF$_2$ and TPA-DAF$_3$-based device are 8.3 and 6.8%, respectively. At the practical brightness of 100 and 1000 cd/m^2, the driving voltages of the TPA-DAF-based device are merely 5.0 and 5.8 V. What's more, it should be noted that TPA-DAF-based device shows a rare slight efficiency roll-off with current efficiency of 20.0 cd/A at 973 cd/m^2, 19.5 cd/A at 5586 cd/m^2, and 17.6 cd/A at 9310 cd/m^2, respectively. That is to say, there is only 12% efficiency roll-off when the luminance increases from 1000 cd/m^2 to 10000 cd/m^2.

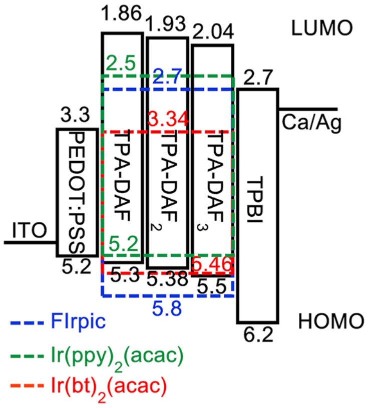


Figure 6. Schematic depicting a comparison of the energy levels of different materials utilized in PhOLEDs.

All the devices show almost identical spectra from the FIrpic dopant with CIE coordinates of (0.20, 0.42), thus indicating that the excitons are entirely confined in the emitting layer. Furthermore, the EL spectra do not show voltage dependence over the whole applied voltage range (Figure S1−S3 in the Supporting Information).

To test the applicability of the hosts as a green phosphorescent emitter, the green phosphorescent material, Ir(ppy)$_2$(acac), was selected as the doped emitter to fabricate green emitting devices with TPA-DAF, TPA-DAF$_2$, and TPA-DAF$_3$ as hosts, respectively. Figure 7 compares *J*−*V*−*L* and CE−*L* curves of those devices with configuration of ITO/PEDOT:PSS (25 nm)/host:Ir(ppy)$_2$(acac) 7 wt % (30 nm)/TPBI (35 nm)/Ca (10 nm)/Ag(100 nm). As shown in Figure 7, green PhOLEDs utilized TPA-DAF, TPA-DAF$_2$, TPA-DAF$_3$ as hosts have the maximum luminance, current efficiency, and EQE of 20854, 13004, and 6882 cd/m^2; 24.5, 26.0, and 17.7 cd/A; and 7.6, 6.7, and 4.9%, respectively. Compared with TPA-DAF$_3$, TPA-DAF, and TPA-DAF$_2$ are more suitable for green PhOLEDs as they had a lower turn-on voltage of 5.5 V and a much higher luminance and current efficiency. Compared to the blue PhOLEDs, the green PhOLEDs show higher turn-on voltages. The reason may lie in that at high doping level, charge trap is more serious in the FIrpic-based device than that in Ir(ppy)$_2$(acac)-based device, and another charge channel forms on dopant molecules.[49] Moreover, the gap of LUMO between FIrpic and TPBI is smaller than that of the green dopant and TPBI. As a result, blue devices show lower turn-on voltages.

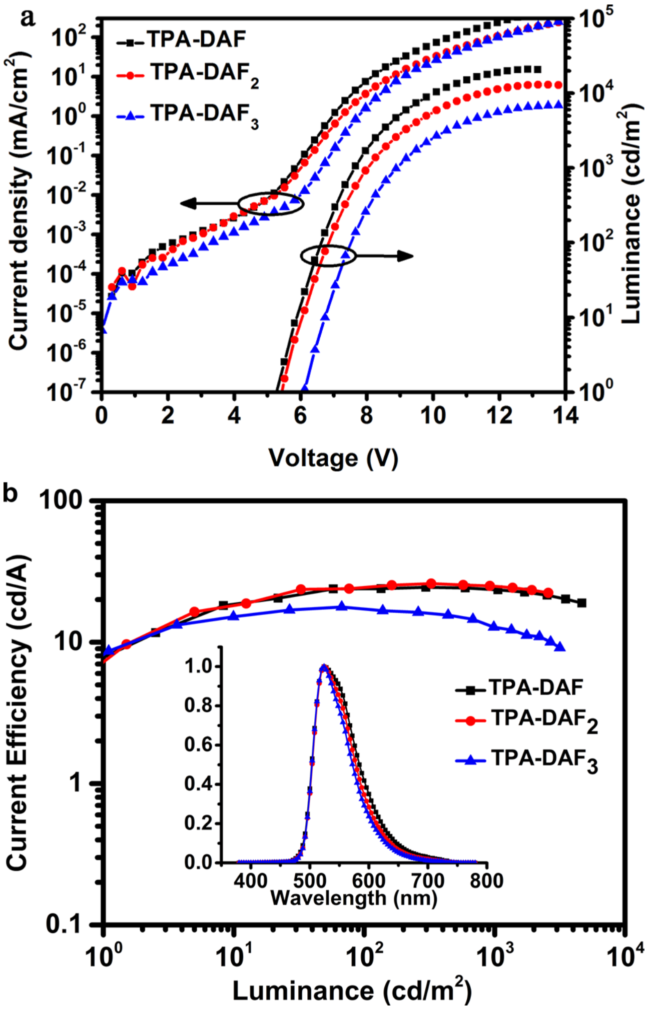


Figure 7. (a) Current density−voltage−luminance; (b) current efficiency−luminance (inset: EL spectrum) with configuration of ITO/PEDOT:PSS (25 nm)/ host:Ir(ppy)$_2$(acac) 7 wt % (30 nm)/ TPBI (35 nm)/Ca (10 nm)/ Ag(100 nm).

To further evaluate the suitability of the compounds as host materials for low energy triplet emitters, we fabricated three red phosphorescent devices (R1−R3) by using TPA-DAF, TPA-DAF_2, TPA-DAF_3 as the hosts, with the same configuration as blue device while using 8 wt % $Ir(bt)_2(acac)$ as the dopant. The performance of these red PhOLEDs is shown in Figure 8.

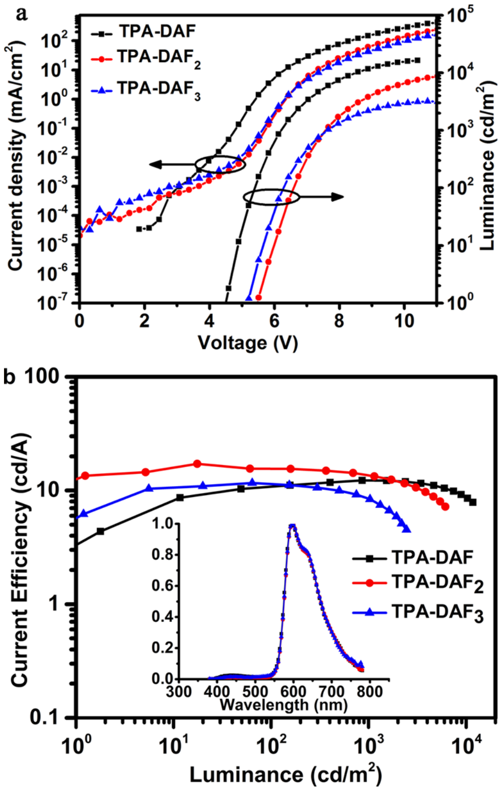


Figure 8. (a) Current density−voltage−luminance; (b) current efficiency−luminance (inset: EL spectrum) with configuration of ITO/PEDOT:PSS (25 nm)/ host:$Ir(bt)_2(acac)$ 7 wt % (30 nm)/ TPBI (35 nm)/Ca (10 nm)/Ag (100 nm).

Devices R1, R2, and R3 exhibit the maximum current efficiency of 12.2, 17.2, and 11.6 cd/A with the maximum luminance of 16670 cd/m^2 at 10.7 V, 9691 cd/m^2 at 12.2 V, and 3190 cd/m^2 at 10.7 V, and maximum EQE of 4.5, 6.5, and 4.6%, respectively. The luminance and current density of device R1 are also much higher than the corresponding results of devices R2 and R3 at the same operating voltage, which further proves the stronger carrier injecting/transporting ability of TPA-DAF compared with TPA-DAF_2 and TPA-DAF_3. As shown in Figure 8, it is noteworthy that device R1 also shows a relatively slight efficiency roll-off with current efficiency of 11.1 cd/A at 156 cd/m^2, 12.2 cd/A at 1526 cd/m^2, 10.5 cd/A at 5995 cd/m^2, and 9.2 cd/A at 8882 cd/m^2, respectively.

All the devices' performance parameters are summarized in Table 2.

CONCLUSION

As a summary, we have presented the comparison of TPA-DAF_n, in which the electron-donor triphenylamine unit was bridged with different ratios of the electron-acceptor 4,5-diazafluorene units using TPA and DAFOH reacted in a sulfuric acid:acetic acid catalytic system. Because the triphenylamine and 4,5-diazafluorene segments were connected through the sp^3-hybridized C9 atom of the 4,5-diazafluorene, thereby eliminating extended p-conjugation, these TPA and DAF hybrids possessed a high triplet energy of 2.88−2.89 eV. Electrochemistry studies and carrier-only devices revealed that the bipolar character of TPA-DAF not only improved the hole injection but also achieved more balanced charge fluxes when compared to those of other two bipolar hosts. As a result, TPA-DAF-based devices showed the best performance with maximum current efficiencies of 20.6, 24.5, and 12.5 cd/A, and maximum EQE of 8.5, 7.6, and 4.5% for blue, green, and red PhOLEDs, respectively. What's more, all TPA-DAF-based devices exhibited a rare slight efficiency roll-off.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details about EL spectra vs voltages of all the devices, optimizations of doping concentration, and thickness of light-emitting layer for the blue, green, and red PhOLEDs. This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: quanyiwu@nju.edu.cn.
*E-mail: iamshye@njupt.edu.cn.
*E-mail: wangy@mail.ipc.ac.cn.
*E-mail: wei-huang@njtech.edu.cn.

Author Contributions

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

Table 2. Performance of OLEDs with Different EMLs

						@ 100 cd/m^2			@ 1000 cd/m^2		
device	V_{on} (V)	L_{max} (cd/m^2)	CE_{max} (cd/A)	PE_{max} (lm/W)	EQE_{max} (%)	CE (cd/A)	PE (lm/W)	CIE	CE (cd/A)	PE (lm/W)	CIE
B1[a]	4.1	21134	20.6	10.9	8.5	16.6	10.5	0.20,0.42	20.1	10.8	0.20,0.42
B2	5.2	8348	20.4	10.5	8.3	19.3	9.6	0.20,0.42	17.6	7.6	0.20,0.43
B3	5.2	6852	16.7	8.5	6.8	16.2	8.2	0.19,0.44	14.0	6.2	0.19,0.43
G1	5.3	20854	24.5	11.6	7.6	23.9	11.3	0.34,0.60	23.6	9.7	0.35,0.60
G2	5.5	13004	26.0	11.5	6.7	24.3	11.2	0.33,0.62	24.8	9.7	0.34,0.62
G3	6.1	6882	17.7	7.6	4.9	17.2	7.2	0.32,0.62	12.7	4.5	0.32,0.62
R1	4.5	16670	12.2	6.3	4.5	10.8	6.3	0.51,0.48	12.2	6.2	0.51,0.48
R2	5.5	9691	17.2	8.8	6.5	15.6	7.4	0.52,0.47	13.5	5.6	0.52,0.48
R3	5.2	3190	11.6	6.0	4.6	11.4	5.7	0.53,0.46	8.5	3.5	0.53,0.47

[a] B, G, R are abbreviations of blue, green, and red and 1, 2, 3 represent the devices utilizing TPA-DAF, TPA-DAF_2, and TPA-DAF_3 as hosts, respectively.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the National Natural Science Foundation of China (21174061, 61106017), the National Key Basic Research Program of China (973 Program, 2014CB648300), the Nature Science Foundation of Jiangsu Province (BK20131375, BM2012010).

ABBREVIATIONS

PhOLEDs, phosphorescent organic light-emitting diodes
TPA, triphenylamine
DAF, diazafluorene
CE, current efficiency
EQE, external quantum efficiency
SCLC, space-charge-limited current

REFERENCES

(1) Baldo, M. A.; O'Brien, D. F.; Shoustikov, Y. Y. A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices. *Nature* **1998**, *395*, 151−154.

(2) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. Recent Progresses on Materials for Electrophosphorescent Organic Light-Emitting Devices. *Adv. Mater.* **2011**, *23*, 926−952.

(3) Huang, B.; Tang, J.; Jiang, W.; Yang, W.; Ban, X.; Sun, Y. Organic Small Molecules Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes. *Chin. J. Org. Chem.* **2013**, *33*, 1395−1406.

(4) Fan, C.; Chen, Y.; Jiang, Z.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. Diarylmethylene-Bridged Triphenylamine Derivatives Encapsulated With Fluorene: Very High Tg Host Materials for Efficient Blue and Green Phosphorescent OLEDs. *J. Mater. Chem.* **2010**, *20*, 3232−3237.

(5) Fu, Q.; Chen, J.; Shi, C.; Ma, D. Solution-Processed Small Molecules as Mixed Host for Highly Efficient Blue and White Phosphorescent Organic Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6579−6586.

(6) Wang, Q.; Wallace, J. U.; Lee, T. Y. H.; Ou, J. J.; Tsai, Y.-T.; Huang, Y.-H.; Wu, C.-C.; Rothberg, L. J.; Chen, S. H. Evaluation of Propylene-, Meta-, and Para-Linked Triazine and Tert-Butyltriphenylamine as Bipolar Hosts for Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2013**, *1*, 2224−2232.

(7) Tao, Y.; Wang, Q.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. Multifunctional Triphenylamine/Oxadiazole Hybrid as Host and Exciton-Blocking Material: High Efficiency Green Phosphorescent OLEDs Using Easily Available and Common Materials. *Adv. Funct. Mater.* **2010**, *20*, 2923−2929.

(8) Ding, J.; Zhang, B.; Lü, J.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. Solution-Processable Carbazole-Based Conjugated Dendritic Hosts for Power-Efficient Blue-Electrophosphorescent Devices. *Adv. Mater.* **2009**, *21*, 4983−4986.

(9) Ye, J.; Chen, Z.; Fung, M.-K.; Zheng, C.; Ou, X.; Zhang, X.; Yuan, Y.; Lee, C.-S. Carbazole/Sulfone Hybrid D-π-A-Structured Bipolar Fluorophores for High-Efficiency Blue-Violet Electroluminescence. *Chem. Mater.* **2013**, *25*, 2630−2637.

(10) Zhuang, J.; Li, W.; Su, W.; Zhou, M.; Cui, Z. Novel Ternary Bipolar Host Material with Carbazole, Triazole and Phosphine Oxide Moieties for High Efficiency Sky-Blue OLEDs. *New J. Chem.* **2014**, *38*, 650−656.

(11) Lin, W.-C.; Huang, W.-C.; Huang, M.-H.; Fan, C.-C.; Lin, H.-W.; Chen, L.-Y.; Liu, Y.-W.; Lin, J.-S.; Chao, T.-C.; Tseng, M.-R. A Bipolar Host Containing Carbazole/Dibenzothiophene for Efficient Solution-Processed Blue and White Phosphorescent OLEDs. *J. Mater. Chem. C* **2013**, *1*, 6835−6841.

(12) Yu, D.; Zhao, F.; Han, C.; Xu, H.; Li, J.; Zhang, Z.; Deng, Z.; Ma, D.; Yan, P. Ternary Ambipolar Phosphine Oxide Hosts Based on Indirect Linkage for Highly Efficient Blue Electrophosphorescence: Towards High Triplet Energy, Low Driving Voltage and Stable Efficiencies. *Adv. Mater.* **2012**, *24*, 509−514.

(13) Zhang, B.; Tan, G.; Lam, C. S.; Yao, B.; Ho, C. L.; Liu, L.; Xie, Z.; Wong, W. Y.; Ding, J.; Wang, L. High-Efficiency Single Emissive Layer White Organic Light-Emitting Diodes Based on Solution-Processed Dendritic Host and New Orange-Emitting Iridium Complex. *Adv. Mater.* **2012**, *24*, 1873−1877.

(14) Lin, W.-C.; Chen, C.-W.; Lin, H.-W. Solution-Processed Organic Light-Emitting Diodes with a Power Efficacy Exceeding 100 lm/W Using Multiple Light Extraction Approaches. *Solid-State Electron.* **2015**, *105*, 58−62.

(15) Lin, W.-C.; Lin, H.-W.; Mondal, E.; Wong, K.-T. Efficient Solution-Processed Green and White Phosphorescence Organic Light-Emitting Diodes Based on Bipolar Host Materials. *Org. Electron.* **2015**, *17*, 1−8.

(16) Jiang, Z.; Chen, Y.; Yang, C.; Cao, Y.; Tao, Y.; Qin, J.; Ma, D. A Fully Diarylmethylene-Bridged Triphenylamine Derivative as Novel Host for Highly Efficient Green Phosphorescent OLEDs. *Org. Lett.* **2009**, *11*, 1503−1506.

(17) Shih, P.-I.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. A Novel Fluorene-Triphenylamine Hybrid That is a Highly Efficient Host Material for Blue-, Green-, and Red-Light-Emitting Electrophosphorescent Devices. *Adv. Funct. Mater.* **2007**, *17*, 3514−3520.

(18) Jiang, Z.; Chen, Y.; Fan, C.; Yang, C.; Wang, Q.; Tao, Y.; Zhang, Z.; Qin, J.; Ma, D. Bridged Triphenylamines as Novel Host Materials for Highly Efficient Blue and Green Phosphorescent OLEDs. *Chem. Commun.* **2009**, 3398−3400.

(19) Chaskar, A.; Chen, H. F.; Wong, K. T. Bipolar Host Materials: A Chemical Approach for Highly Efficient Electrophosphorescent Devices. *Adv. Mater.* **2011**, 23, 3876−3895.

(20) Zheng, Y.; Batsanov, A. S.; Jankus, V.; Dias, F. B.; Bryce, M. R.; Monkman, A. P. Bipolar Molecules with High Triplet Energies: Synthesis, Photophysical, and Structural Properties. *J. Org. Chem.* **2011**, *76*, 8300−8310.

(21) Tao, Y.; Wang, Q.; Shang, Y.; Yang, C.; Ao, L.; Qin, J.; Ma, D.; Shuai, Z. Multifunctional Bipolar Triphenylamine/Oxadiazole Derivatives: Highly Efficient Blue Fluorescence, Red Phosphorescence Host and Two-Color Based White OLEDs. *Chem. Commun.* **2009**, 77−79.

(22) Linton, K. E.; Fisher, A. L.; Pearson, C.; Fox, M. A.; Pålsson, L.-O.; Bryce, M. R.; Petty, M. C. Colour Tuning of Blue Electroluminescence Using Bipolar Carbazole−Oxadiazole Molecules in Single-Active-Layer Organic Light Emitting Devices (OLEDs). *J. Mater. Chem.* **2012**, *22*, 11816−11825.

(23) Huang, H.; Wang, Y.; Pan, B.; Yang, X.; Wang, L.; Chen, J.; Ma, D.; Yang, C. Simple Bipolar Hosts with High Glass Transition Temperatures Based on 1,8-Disubstituted Carbazole for Efficient Blue and Green Electrophosphorescent Devices with "Ideal" Turn-On Voltage. *Chem.—Eur. J.* **2013**, *19*, 1828−1834.

(24) Gong, S.; Fu, Q.; Wang, Q.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. Highly Efficient Deep-Blue Electrophosphorescence Enabled by Solution-Processed Bipolar Tetraarylsilane Host with Both a High Triplet Energy and a High-Lying HOMO Level. *Adv. Mater.* **2011**, *23*, 4956−1959.

(25) Shao, S.; Ding, J.; Ye, T.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. A Novel, Bipolar Polymeric Host for Highly Efficient Blue Electrophosphorescence: A Non-Conjugated Poly(aryl ether) Containing Triphenylphosphine Oxide Units in the Electron-Transporting Main Chain and Carbazole Units in Hole-Transporting Side Chains. *Adv. Mater.* **2011**, *23*, 3570−3574.

(26) Lee, Y.-T.; Chang, Y.-T.; Lee, M.-T.; Chiang, P.-H.; Chen, C.-T.; Chen, C.-T. Solution-Processed Bipolar Small Molecular Host Materials for Single-Layer Blue Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2014**, *2*, 382−391.

(27) Han, C.; Xie, G.; Xu, H.; Zhang, Z.; Xie, L.; Zhao, Y.; Liu, S.; Huang, W. A Single Phosphine Oxide Host for High-Efficiency White Organic Light-Emitting Diodes with Extremely Low Operating Voltages and Reduced Efficiency Roll-Off. *Adv. Mater.* **2011**, *23*, 2491−2496.

(28) Yang, X.; Huang, H.; Pan, B.; Aldred, M. P.; Zhuang, S. Q.; Wang, L.; Chen, J. S.; Ma, D. Modified 4,4′,4″-Tri(N-carbazolyl)-triphenylamine as a Versatile Bipolar Host for Highly Efficient Blue, Orange, and White Organic Light-Emitting Diodes. *J. Phys. Chem. C* **2012**, *116*, 15041−15047.

(29) Lee, C. W.; Lee, J. Y. High Quantum Efficiency in Solution and Vacuum Processed Blue Phosphorescent Organic Light Emitting Diodes Using a Novel Benzofuropyridine-Based Bipolar Host Material. *Adv. Mater.* **2013**, *25*, 596−600.

(30) Lee, C. W.; Kim, J. K.; Joo, S. H.; Lee, J. Y. High Quantum Efficiency Blue Phosphorescent Organic Light-Emitting Diodes Using 6-Position-Modified Benzofuro[2,3-B] Pyridine Derivatives. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2169−2173.

(31) Gong, S.; Chen, Y.; Luo, J.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. Bipolar Tetraarylsilanes as Universal Hosts for Blue, Green, Orange, and White Electrophosphorescence with High Efficiency and Low Efficiency Roll-Off. *Adv. Funct. Mater.* **2011**, *21*, 1168−1178.

(32) Chen, H.; Jiang, Z. Q.; Gao, C. H.; Xu, M. F.; Dong, S. C.; Cui, L. S.; Ji, S. J.; Liao, L. S. Silicon-Based Material with Spiro-Annulated Fluorene/Triphenylamine as Host and Exciton -Blocking Layer for Blue Electrophosphorescent Devices. *Chem.—Eur. J.* **2013**, *19*, 11791−11797.

(33) Zheng, C.-J.; Ye, J.; Lo, M.-F.; Fung, M.-K.; Ou, X.-M.; Zhang, X.-H.; Lee, C.-S. New Ambipolar Hosts Based on Carbazole and 4,5-Diazafluorene Units for Highly Efficient Blue Phosphorescent OLEDs with Low Efficiency Roll-Off. *Chem. Mater.* **2012**, *24*, 643−650.

(34) Chen, H.-F.; Wang, T.-C.; Hung, W.-Y.; Chiu, H.-C.; Yun, C.; Wong, K.-T. Spiro-Configured Bipolar Hosts Incorporating 4,5-Diazafluroene as the Electron Transport Moiety for Highly Efficient Red and Green Phosphorescent OLEDs. *J. Mater. Chem.* **2012**, *22*, 9658.

(35) Wong, K.-T.; Chen, R.-T.; Fang, F.-C; Wu, C-c; Lin, Y.-T. 4,5-Diazafluorene-Incorporated Ter(9,9-diarylfluorene): A Novel Molecular Doping Strategy for Improving the Electron Injection Property of a Highly Efficient OLED Blue Emitter. *Org. Lett.* **2005**, *7*, 1979−1982.

(36) Yook, K. S.; Lee, J. Y. Small Molecule Host Materials for Solution Processed Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* **2014**, *26*, 4218−4233.

(37) Jiang, W.; Duan, L.; Qiao, J.; Dong, G.; Wang, L.; Qiu, Y. Tuning of Charge Balance in Bipolar Host Materials for Highly Efficient Solution-Processed Phosphorescent Devices. *Org. Lett.* **2011**, *13*, 3146−3149.

(38) Jiang, W.; Yang, W.; Ban, X.; Huang, B.; Dai, Y.; Sun, Y.; Duan, L.; Qiu, Y. Synthesis of New Bipolar Materials Based on Diphenylphosphine Oxide and Triphenylamine Units: Efficient Host for Deep-Blue Phosphorescent Organic Light-Emitting Diodes. *Tetrahedron.* **2012**, *68*, 9672−9678.

(39) Evanoff, D. D., Jr.; Lawrence, J. R.; Huebner, C. F.; Houchins, J. M.; Stevenson, B. J.; Foguth, A. L.; Carroll, J. B.; Foulger, S. H. Copolymers of 2-(9H-Carbazol-9-Yl)Ethyl 2-Methylacrylate and 4-[5-(4-Tert-Butylphenyl)-1,3,4-Oxadiazol-2-Yl]Phenyl 2-Methylacrylate: Correlating Hole Drift Mobility and Electronic Structure Calculations with Electroluminescence. *ACS Appl. Mater. Interfaces* **2009**, *1*, 875−881.

(40) Cheng, S.-H.; Chou, S.-H.; Hung, W.-Y.; You, H.-W; Chen, Y.-M.; Chaskar, A.; Liu, Y.-H.; Wong, K.-T. Fine-Tuning the Balance between Carbazole and Oxadiazole Units in Bipolar Hosts to Realize Highly Efficient Green PhOLEDs. *Org. Electron.* **2013**, *14*, 1086−1093.

(41) Jeon, S. O.; Yook, K. S.; Joo, C. W.; Lee, J. Y. Phenylcarbazole-Based Phosphine Oxide Host Materials for High Efficiency in Deep Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Funct. Mater.* **2009**, *19*, 3644−3649.

(42) Li, N. Q.; Chen, Q.; Fan, Z. K.; Quan, Y. W.; Chen, Q. M. Synthesis and Characterization of Bipolar Hosts Based on Triphenylamine and 4,5-Diazafluorene Through Friedel-Crafts Reaction. *Curr. Org. Synth.* **2015**, *12*, 71−75.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M. N.; Honda, T. Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *GAUSSIAN 09, Revision A.1*; GAUSSIAN, Inc.: Wallingford CT, 2009.

(44) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(45) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785−789.

(46) Baldacchini, G.; Baldacchini, T.; Chiacchiaretta, P.; Pode, R. B.; Vincenti, M. A.; Wang, Q.-M. Why Annealing Processes Affect the Optical Properties of Alq3 Films and OLEDs. *ESC Trans.* **2009**, *16*, 3−9.

(47) Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Masciocchi, N.; Sironi, A. Correlation between Molecular Packing and Optical Properties in Different Crystalline Polymorphs and Amorphous Thin Films of *mer*-Tris(8-hydroxyquinoline)aluminum-(III). *J. Am. Chem. Soc.* **2000**, *122*, 5147−5157.

(48) Han, C.; Zhao, Y.; Xu, H.; Chen, J.; Deng, Z.; Ma, D.; Li, Q.; Yan, P. A Simple Phosphine-Oxide Host with a Multi-Insulating Structure: High Triplet Energy Level for Efficient Blue Electrophosphorescence. *Chem.—Eur. J.* **2011**, *17*, 5800−5803.

(49) Holmes, R. J.; D'Andrade, B. W.; Forrest, S. R.; Ren, X.; Li, J.; Thompson, M. E. Efficient, Deep-Blue Organic Electrophosphorescence by Guest Charge Trapping. *Appl. Phys. Lett.* **2003**, *83*, 3818−3820.

DOI: 10.1021/am509014v
ACS Appl. Mater. Interfaces 2015, 7, 9445−9452