ACS APPLIED MATERIALS & INTERFACES
Research Article
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Highly Simplified Reddish Orange Phosphorescent Organic Light-Emitting Diodes Incorporating a Novel Carrier- and Exciton-Confining Spiro-Exciplex-Forming Host for Reduced Efficiency Roll-off

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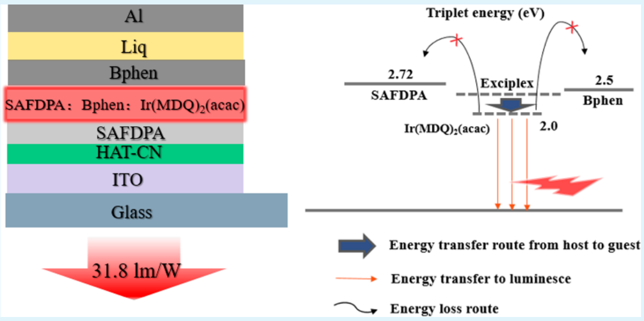
Supporting Information



ABSTRACT: A novel exciplex-forming host is applied so as to design highly simplified reddish orange light-emitting diodes (OLEDs) with low driving voltage, high efficiency, and an extraordinarily low efficiency roll-off, by combining *N*,*N*-10-triphenyl-10*H*-spiro [acridine-9,9′-fluoren]-3′-amine (SAFDPA) with 4,7-diphenyl-1,10-phenanthroline (Bphen) doped with trivalent iridium complex bis(2-methyldibenzo[f,h]-quinoxaline) (acetylacetonate)iridium(III) ($Ir(MDQ)_2(acac)$). The reddish orange OLEDs achieve a strikingly high power efficiency (PE) of 31.80 lm/W with an ultralow threshold voltage of 2.24 V which is almost equal to the triplet energy level of the phosphorescent reddish orange emitting dopant. The power efficiency of the device with the exciplex-forming host is enhanced, achieving 36.2% mainly owing to the lower operating voltage by the novel exciplex forming cohost, compared with the reference device (23.54 lm/W). Moreover, the OLEDs show extraordinarily low current efficiency (CE) roll-off to 1.41% at the brightness from 500 to 5000 cd/m^2 with a maximal CE of 32.87 cd/A (EQE_{max} = 11.01%). The devices display a good reddish orange color (CIE of (0.628, 0.372) at 500 cd/m^2) nearly without color shift with increasing brightness. Co-host architecture phosphorescent OLEDs show a simpler device structure, lower working voltage, and a better efficiency and stability than those of the reference devices without the cohost architecture, which helps to simplify the OLED structure, lower the cost, and popularize OLED technology.

KEYWORDS: *OLED, reddish orange phosphorescence, exciplex-forming host, hole-transport-material-free, efficiency roll-off*

1. INTRODUCTION

Nowadays, organic light emitting diodes (OLEDs) are exhibiting distinguished characteristics, for instance, extensive viewing angles, striking color rendering, physiologically friendly, easily fabricating large-area plane light source, and flexiblility.[1−8] The rapid progress of red light occupying the wavelength from 600 to 700 nm helps to solve environmental issues in artificial illumination of agricultural and medical treatment.[9,10] Meanwhile, red color is an important one of the three primary colors of OLEDs for flat-panel displays, and reddish orange OLEDs play an important role as complementary color devices in white solid-state lightings. Until today, an enormous effort has been made to demonstrate state-of-the-art red phosphorescent OLEDs (PhOLEDs) with both good stability and high power efficiency (PE). In the perspective of a novel material, a lot of host materials with high triplet energy level (T1) of red phosphorescent dopants have been fabricated by the Ma group with a high current efficiency (CE) of 22 cd/A (EQE_{max} = 7.8%).[11,12] Then, Chou and co-workers[13] reported an efficiency of 21.3 cd/A (EQE_{max} = 15.3%) with charge-neutral Os(II) emitters. Jou et al. reported a high CE of 44.8 cd/A (EQE_{max} = 19.7%) at 1000 cd/m^2 with iridium complexes as the host.[14−16] Moreover, some novel phosphorescent hosts FPPCA, BZQPG, and FPYPCA possessing bipolar charge transporting ability realize record-efficiency orange-red and deep-red PhOLEDs with very high-level CE > 50 cd/A (EQE >

Received: October 14, 2016
Accepted: December 30, 2016
Published: December 30, 2016

DOI: 10.1021/acsami.6b13077
ACS Appl. Mater. Interfaces 2017, 9, 2701−2710

23%), as reported by Wang's and Liu's group.[17,18] To lower the working voltage, the p-doping and n-doping lower the injection energy gap and improve the carrier conduction by mixed with acceptors or donors as the hole conducting materials or electron conducting materials, respectively.[19,20] With the same effect, syntheses of new materials with proper energy levels and high mobility were known to lower the operating voltage.[21−24] Shu's group reported a CE of 29.2 cd/A with a fluorene-triphenylamine host material, Chi and Shu's groups reported a CE of 32.8 cd/A at 1000 cd/m^2 by incorporating a fluorene-based bipolar host material,[25,26] and Pode's group developed a red OLED with a CE of 26.5 cd/A at 1000 cd/m^2 by application of an ideal host−guest system.[27] Zhang et al. improved properties of platinum II (PtII) complex by codoping the Ir^{III} complex into the light-emitting layer (EML) as a novel energy band structure to realize efficient conversion and utilization of exciton energy.[28,29] Moreover, the reddish orange emitter has been applied into novel white OLEDs to attain fine charge balance and exciton confinement in EMLs.[30,31]

Furthermore, spiro-based exciplex-forming hosts, instead of hole or electron conduction single hosts, have been developed to realize good charge equilibrium without electrical loss in conventional fluorescent and phosphorescent OLEDs.[32−34] Generally, multiple carrier transport layers are needed to favorably transport carriers by matching the molecular orbital energy level in OLEDs.[4] An extra hole transport layer (HTL) is also applied and introduces an additional interface,[35,36] with the most common examples being thin films 1,1-bis[4-[*N*,*N*-di(*p*-tolyl)-amino]phenyl] cyclohexane) (TAPC), which significant decreases the drive voltage.[23,37] However, an extra layer needed to balance carrier transport[38] and lower the charge transport barrier largely increases the manufacturing cost and also brings extra heterojunctions into the OLEDs which usually are detrimental to its stability. Thus, there is urgently needed to simplify the OLEDs structure and fabrication procedure. Therefore, multifunctional novel organic materials are required that can be a hole transport layer (HTL) and host layer at the same time. Previously, spiro[fluorene-benzofluorene]-type host materials for reddish orange PhOLEDs are seldom reported[16] compared with other PhOLEDs and TADF (thermally activated delayed fluorescence) characteristics.[39,40] Also, spiro-based hole transport materials were applied in high efficiency polymer or perovskite solar cells showing excellent performance.[41−43] However, seldom researchers paid attention to apply spiro-based organic materials as the host and HTL simultaneously as a sally port to simplify the device structure and fabrication process of PhOLEDs without sacrificing device performance.

On the other hand, CE roll-off is one of the most usual weaknesses of PhOLEDs, which may limit their implementation at high brightness in lighting applications.[24] Triplet−triplet annihilation (TTA), triplet−polaron quenching (TPQ), and field-induced quenching are possible quenching processes in OLEDs.[34] Baldo et al.[44] reported that TTA is the primary reason that caused the CE roll-off of OLEDs, while Reineke et al.[45] hold the opinion that both TTA and TPQ should be considered for common OLEDs. Moreover, it is required to reduce the impact such as concentration quenching and triplet−triplet annihilation to lower the efficiency roll-off. A mixed host architecture helps to lower the efficiency roll-off of OLEDs, but few researchers have applied a mixed host into orange-red PhOLEDs.[30]

To address these two issues at the same time, an effective and synergetic strategy to design OLEDs is proposed for reducing the number of layers in OLEDs without sacrificing device performance while reducing CE roll-off by a carrier- and exciton-confining spiro-exciplex-forming host. The following rules are required for a highly simplified exciplex-forming host for novel PhOLEDs: (1) A suitable lowest unoccupied molecular orbital (LUMO) level of HTL, collocating work function (WF) of ITO anode, in conventional OLEDs, for the sake of avoiding requirements for multiple transport layers. (2) T1 level of donor and acceptor of an exciplex-forming host should exceed the T1 level of a phosphorescent guest to confine the limited-range recombination zone and realize the energy transduction from the exciplex-forming host to a red guest. (3) Deeper HOMO (highest occupied molecular orbital) of ETL (electron transport layer) and higher LUMO of spiro-series materials confining the exciton recombination zone to avoid quenching during charge transport.

Herein, we report a novel exciplex-forming host architecture by combining *N*,*N*-10-triphenyl-10*H*-spiro[acridine-9,9′-fluoren]-3′-amine (SAFDPA) with 4,7-diphenyl-1,10-phenanthroline (Bphen) to explore common electron transport materials and further apply to a highly simplified orange-red phosphorescence OLED structure. A suitable LUMO of SAFDPA matches the WF of the ITO anode of conventional OLEDs to avoid the requirement for multiple transport layers. Moreover, the T1 level of the exciplex is higher than that of the trivalent iridium complex bis(2-methyldibenzo[f,h]quinoxaline)(acetylacetonate)iridium(III) (Ir(MDQ)$_2$(acac)) (2.0 eV) so that energy transfers to a reddish orange dopant of Ir(MDQ)$_2$(acac). Furthermore, the designed OLEDs with reddish orange emission and using SAFDPA:Bphen (1:1, w:w) mixed host architecture annihilating additional hole transport material show a simpler device structure with deeper HOMO of Bphen and higher LUMO of SAFDPA confining the exciton recombination zone to avoid quenching during the process of transportation. Lower working voltage, better efficiency, and stability are achieved compared with the reference device applying 1-bis[4-[*N*,*N*-di(4-tolyl)amino]phenyl]-cyclohexane (TAPC) as the hole transport layer without the cohost architecture. Particularly, the designed reddish orange OLEDs achieve a strikingly high power efficiency (PE) of 31.80 lm/W with an ultralow turn-on voltage of 2.24 V which is almost equal to the triplet energy level of the phosphorescent reddish orange emitting dopant. The power efficiency of the device with exciplex-forming host is enhanced, achieving 36.2% mainly owing to the lower operating voltage by the novel exciplex forming cohost, compared with the reference device (23.54 lm/W). Moreover, the OLEDs show an extraordinarily low CE roll-off to 1.41% at the brightness from 500 to 5000 cd/m^2 with the maximal CE of 32.87 cd/A (EQE$_{max}$ = 11.01%). The devices display a good reddish orange color (CIE of (0.628, 0.372) at 500 cd/m^2) nearly without color shift with increasing brightness. An effective and synergetic strategy is provided to design highly simplified reddish orange PhOLEDs with low efficiency roll-off, which helps to lower the cost and popularize OLED technology.

2. EXPERIMENTAL SECTION

Chemical structures of all materials used are exhibited in Figures 1 and 2. 1,4,5,8,9,11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN), 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi), bathocuproine (BCP), 1,3,5-tri[(3-pyridyl)-phen-3-yl] benzene

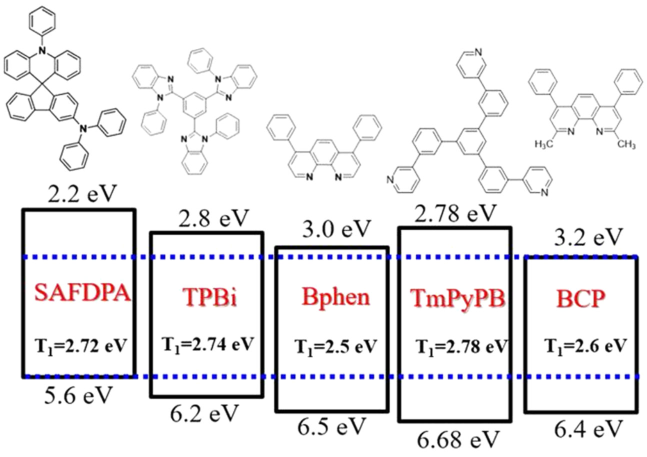


Figure 1. Energy band and triplet energy level diagram of SAFDPA and common ETL materials with their chemical structures shown above.

(TmPyPB), 4,7-diphenyl-1,10-phenanthroline (Bphen), Ir-(MDQ)$_2$(acac), TAPC, and 8-hydroxyquinolinolatolithium (Liq) were purchased from Lumtec Company and used as received. SAFDPA was synthesized according to the literature from our cooperative partner.[46]

All OLED devices were fabricated on patterned indium−tin−oxide (ITO) substrates with a sheet resistance of 15 Ω/square. The ITO glasses were cleaned in a sequent sonication bath of acetone and isopropanol for 10 min one by one and after that blow-dried by a nitrogen gun and treated in a UV-ozone chamber for 15 min in the end. After UV-ozone, the substrates were placed in the vacuum cavity for OLED fabrication. The multilayers such as inorganic layers, organic EL layers, and electrode materials were orderly grown on the ITO substrates without breaking the vacuum[6] ($\sim 5.0 \times 10^{-6}$ Torr). The growth rates of organic layers, Liq, and Al were about 1, 0.1, and 5 Å/s, respectively. The deposition rates were tested by quartz crystals. The practical OLED area was fabricated by the overlap of the ITO anode and the Al cathode was 3 mm × 3 mm.[6]

Charge balance is one of the four most important factors affecting OLED performance: EQE = charge balance factor × exction emission rate × optical out-coupling factor × PL efficiency. To get fair OLED performance, one needs to optimize the thickness of HTL and ETL to make sure that the charge carrier recombination zone is located in the emission zone of the luminescent materials. On the basis of the above-mentioned understanding of the design philosophy of OLEDs, in our reference devices, ITO/HAT-CN (10 nm)/TAPC (45 nm)/SAFDPA:Ir(MDQ)$_2$(acac) (1, 2, 6, and 8 wt %; 20 nm)/Bphen (50 nm)/Liq (2 nm)/Al (120 nm), the thickness of each functional layer is repeatedly optimized to reach fine charge balance factor.[46] Likewise, in our designed devices, ITO/HAT-CN (10 nm)/SAFDPA (25, 35, and 45 nm)/cohost:Ir(MDQ)$_2$(acac) (2 wt %, 20 nm)/Bphen (45 nm)/Liq (2 nm)/Al (120 nm), the thickness of SAFDPA as a variable value is optimized to reach fine charge balance factor. The mixed cohost layer of SAFDPA:Bphen (1:1, w:w) in the designed devices helps to achieve a better charge balance in the EML,[47] which can be easily tuned by controlling the ratio of the electron and hole transport materials. As the hole mobility of SAFDPA ($\sim 5.65 \times 10^{-4}$ cm^2/(V s)) and the electron mobility of Bphen ($\sim 3.9 \times 10^{-4}$ cm^2/(V s)) are very close, we therefore fabricate OLEDs using a SAFDPA:Bphen (1:1, w:w) mixed host. The energy band structures of the fabricated OLEDs are exhibited in Figure 2. HAT-CN and TAPC play roles as a hole injection layer (HIL) and a hole transportion layer (HTL), respectively, while Liq and Bphen play roles as an electron injection layer (EIL) and an electron transportion layer (ETL), respectively. In PhOLED devices E, F, and G, SAFDPA:Bphen is applied as an exciplex-forming host and Ir(MDQ)$_2$(acac) as a dopant. However, in devices A, B, C, and D, a conventional host−dopant emitting system of SAFDPA and Ir(MDQ)$_2$(acac) is applied with different doping rates to optimize the reference device.

The current density−voltage (*J*−*V*) and electroluminescence (EL) properties were tested by a photometer (Photo Research SpectraScan PR 655) assembed with a constant-current source (Keithley 2400 sourcemeter).[48] Photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (Hitachi F-4600). Delayed PL emission was recorded on an ultrafast fluorescence spectrometer (HORIB-FM-2015). All above tests were done under room temperature conditions and exposed to ambient air without any protective coats. The operational stability (or lifetime), of the devices packaged in air, was tested at a started brightness of 3000 cd/m^2 and at room temperature. The EL intensity and lifetime of OLEDs were kept a record by a computer until the testing finished.[49]

3. RESULTS AND DISCUSSION

Photoluminescence spectra of SAFDPA, common electron transport materials (Bphen, BCP, TmPyPB, TPBi), and mixed films are tested, as exhibited in Figure 3. These electron transporters also act as hole blocking layers (BCP 6.4 eV, TPBI 6.2 eV, TmPyPB 6.68 eV, and BPhen 6.5 eV) compared with the HOMO level (5.6 eV) of SAFDPA, as exhibited in Figure 1.

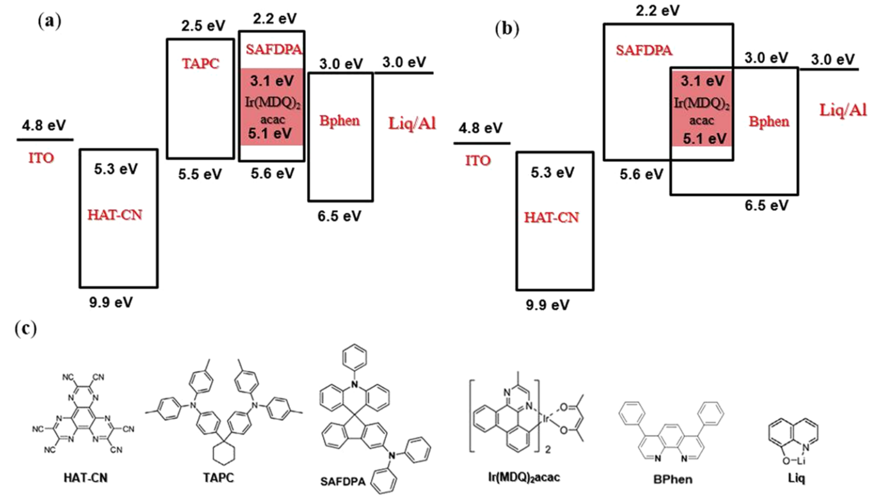


Figure 2. Energy band diagram and device structures of (a) reference device and (b) designed device with novel exciplex-forming host and (c) chemical structures of organic materials used to fabricate the designed devices.

DOI: 10.1021/acsami.6b13077
ACS Appl. Mater. Interfaces 2017, 9, 2701−2710

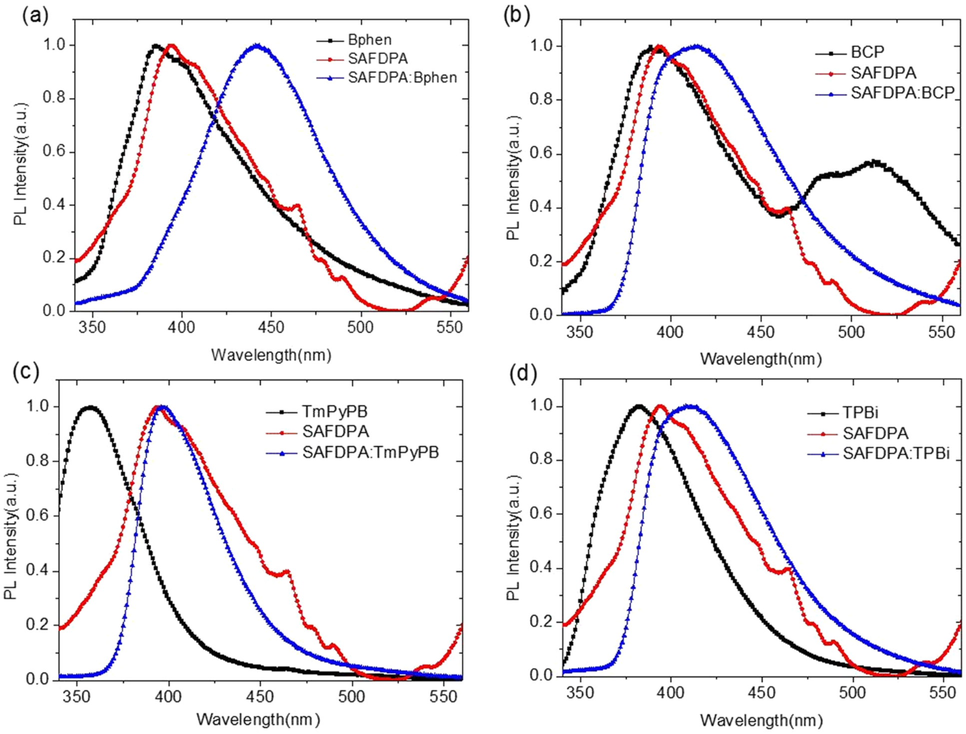


Figure 3. PL spectra of (a) Bphen, SAFDPA, and mixed SAFDPA:Bphen (1:1, w:w) films; (b) BCP, SAFDPA, and mixed SAFDPA:BCP (1:1, w:w); (c) TmPyPB, SAFDPA, and mixed SAFDPA:TmPyPB (1:1, w:w); and (d) TPBi, SAFDPA, and mixed SAFDPA:TPBi (1:1, w:w) (all films are 30 nm thick and tested at room temperature).

The exciplex emission generally comes from the delocalization of electronic excitation over the two kinds of molecules and from partial electron transfer between the electron-donating and electron-accepting molecules. The charge transfer properties of the exciplex are mainly dependent on the strength of the electron-donating properties of the donor materials and on the electron affinity of the acceptor.[50] Thus, it is reasonably inferred that the formation of exciplex emission in SAFDPA is owing to the electron-donating ability of SAFDPA resulting from the fluorene moiety. Although TmPyPB has more excellent electron transport capability than Bphen, BCP, and TPBi, no red-shift PL peak from exciplex is observed, suggesting that the exciplex cannot be formed between SAFDPA and TmPyPB, as exhibited in Figure 3c. An additional exciplex peak is observed in the thin films of SAFDPA mixed with the electron-accepting material (BPhen, TPBi, and BCP), providing the possibility to get a spiro-exciplex-forming host-based device, as exhibited in Figure 3. The higher LUMO level of SAFDPA (2.2 eV) leads to the possibility of acting as an electron blocking layer and forming exciplex-forming host, simultaneously. Moreover, so as to discuss the carrier transport properties of SAFDPA and TAPC, we fabricate and discuss hole-only devices: ITO/MoO3 (10 nm)/TAPC or SAFDPA (100 nm)/MoO3 (10 nm)/Al (100 nm). The *J*−*V* properties of the devices are exhibited in Supporting Information Figure S1. The hole mobility of SAFDPA is ~5.65 × 10^{-4} $cm^2/(V\ s)$, which is high enough to form good charge balance compared with Bphen (electron mobility = 3.9 × 10^{-4} $cm^2/(V\ s)$). Moreover, the hole mobility of SAFDPA is comparable with other SAF-series materials.[51,52]

In the perspective of electron-transport capability, TmPyPB is one of the best commercial small-molecule electron-transport materials (ETMs) among Bphen, BCP, TPBi, and TmPyPB. The electron mobilities of Bphen, BCP, TPBi, and TmPyPB are 3.9 × 10^{-4}, 6 × 10^{-7}, 3.3 × 10^{-5}, and 1 × 10^{-3} $cm^2/(V\ s)$, respectively.[53−56] The distinguished electron mobility lets us choose TmPyPB as the first choice as ETMs in designed OLEDs. Moreover, as seen in our cooperator's paper,[46] the higher efficiency of the devices is mainly owed to the reason that TmPyPB was applied in the OLEDs promoting charge transport balance (TAPC with a hole mobility of 1.00 × 10^{-2} $cm^2/(V\ s)$[57]). Unfortunately, the PL spectra of mixed SAFDPA:TmPyPB without a red shift suggest that this mixed system does not form an exciplex-forming host. The PL spectra of mixed SAFDPA:Bphen, SAFDPA:BCP, and SAFDPA:TPBi film showing more or less a red shift imply existing exciplex energy interaction between SAFDPA and ETMs (Bphen, BCP, and TPBi), and Bphen possesses the highest electron mobility among them which helps to enhance the charge transport balance of OLEDs. Therefore, we have chosen SAFDPA:Bphen as the exciplex-forming host to design and fabricate OLEDs to primely demonstrate our OLED design strategy. Moveover, we fabricate reference OLEDs with SAFDPA:TmPyPB as non-exciplex-forming cohost OLEDs shown in Figure S1 of the Supporting Information to effectively support our viewpoints.

The PL spectra of SAFDPA, BPhen, and SAFDPA:BPhen = 1:1 (w:w) codeposited films are exhibited in Figure 3a. The mixture of SAFDPA:BPhen with 1:1 (w:w) exhibits violet blue emission with a peak at 438 nm. The energy of this peak (~2.8 eV) nearly corresponds to the offset between the LUMO of BPhen (~3.0 eV) and the HOMO of SAFDPA (~5.6 eV), verifying that the luminescence arises from exciplex emission. The mixture of SAFDPA:BCP exhibits violet blue emission with a peak at 413 nm, as exhibited in Figure 3b. This peak energy (~3.0 eV) hardly corresponds to the offset between the LUMO of BCP (~3.0 eV) and the HOMO of SAFDPA (~5.6 eV). The PL spectra of BCP (Figure 3b) show secondary peaks at 520 nm owing to the effect of excimers, dimers, or other aggregates[58] which destroy by doping SAFDPA. The PL spectra of mixture films of SAFDPA:TmPyPB of 1:1 (w:w) do not show the red shift relative to the PL spectrum of SAFDPA, as exhibited in Figure 3c. The mixture of SAFDPA:TPBi exhibits violet blue emission with a peak at 413 nm, as exhibited in Figure 3d. The peak energy (~3.0 eV) hardly corresponds to the energy offset between the LUMO of TPBi (~3.0 eV) and the HOMO of SAFDPA (~5.6 eV). The PL spectra of SAFDPA:BCP and SAFDPA:TPBi imply that the mixture may not form exciplex emission. Figure 4 shows delayed PL emission intensity of mixed SAFDPA:TmPyPB (1:1, w:w) films and mixed SAFDPA:Bphen (1:1, w:w) films, which indicate that the exciton lifetime of the SAFDPA:Bphen cohost is remarkably longer than the exciton lifetime of SAFDPA:TmPyPB films, supporting the formation of SAFDPA:Bphen exciplex emission. One leaf is not the same as another (exciplex-forming systems)[59−61] in the world; even so, we find a similar and comparable known exciplex-forming system: TCTA:B3PYMPM, to our SAFDPA:Bphen, which can be used to design high efficiency exciplex emission OLEDs.[62] Moreover, SAFDPA:Bphen has a suitable energy state following three rules proposed in the Introduction: (1) A suitable lowest unoccupied molecular orbital (LUMO) level of SAFDPA, matching WF of ITO anode, in conventional OLEDs, for the purpose of avoiding the requirement for multiple transport layers (TAPC). (2) T1 levels of SAFDPA and Bphen are higher than that of a red phosphorescent dopant to confine the recombination zone and utilize the energy transfer from the exciplex to the dopant. (3) Deeper HOMO (highest occupied molecular orbital) of Bphen and higher LUMO of SAFDPA confining the exciton recombination zone to avoid quenching during charge transport. Therefore, we design PhOLEDs based on the characteristics of a novel exciplex-forming host to simplify device structure and enhance the performance of devices.

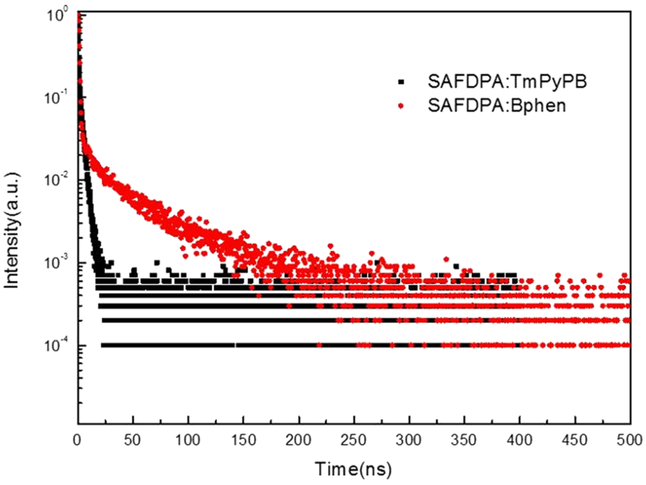


Figure 4. Delayed PL emission intensity of mixed SAFDPA:TmPyPB (1:1, w:w) and mixed SAFDPA:Bphen (1:1, w:w) thin films. Dependence on laser pulse fluence at room temperature. Recorded from 0 to 500 ns.

To optimize the reference device performance, among devices A, B, C, and D, the doping proportion of Ir(MDQ)$_2$(acac) into SAFDPA was decreased from 8% (device D) to 1% (device A) (device B, 2 wt %; device C, 6 wt %) on the basis of the previously reported guest−host red PhOLED research.[63,64] The current density−voltage−luminance (*J*−*V*−*L*) characteristics, efficiency, and EL spectra of reference devices are exhibited in Figure 5. As exhibited in Figure 5a and d, *J*−*V* characteristics and normalized EL spectra show tiny

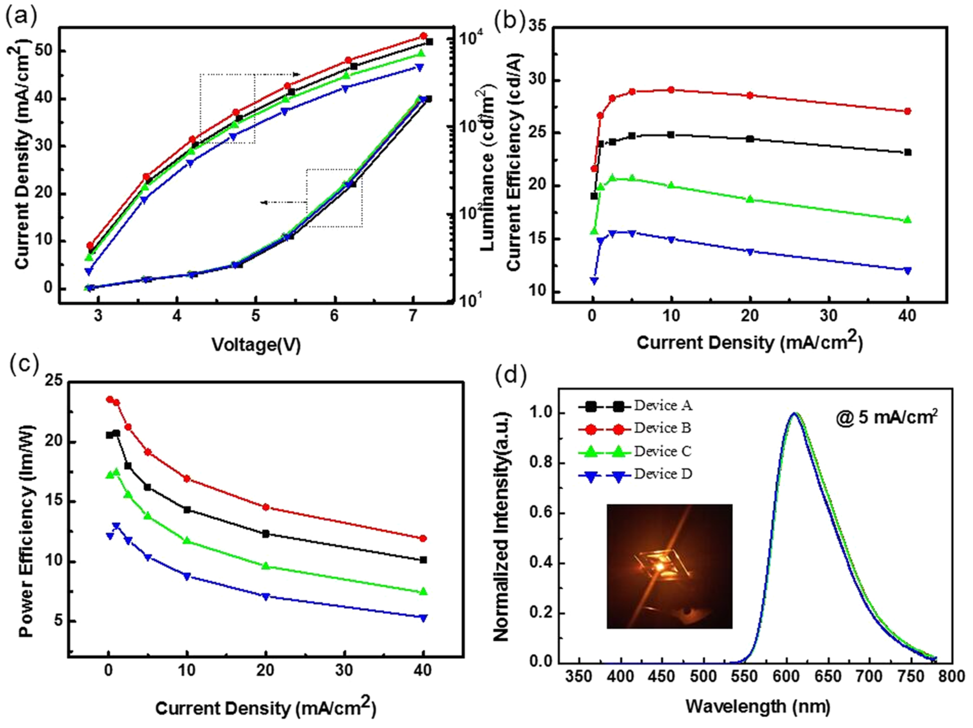


Figure 5. (a) Current density−voltage−-luminance characteristics of reference devices. (b) Current efficiency−current density characteristic of reference devices. (c) Power efficiency−current density characteristic of reference devices. (d) Normalized EL spectra of reference devices.

Table 1. Performance Summary of the Reference Red PhOLEDs

device[a]	voltage (V)[b]	η_c[c] (cd/A)	η_p (lm/W)[c](EQE)[c]	emission peak (nm)	CIE[d]	roll-off[e] (%), 500−5000 cd/m^2
A	2.91	24.87	20.72 (8.33%)	608	0.627, 0.372	4.3
B	2.88	29.09	23.54 (9.74%)	608	0.626, 0.372	6.3
C	2.87	20.68	17.41 (6.92%)	608	0.631, 0.367	19.1
D	2.86	15.61	13.07 (5.23%)	608	0.631, 0.368	22.7

[a] The reference PhOLEDs with different doping proportions of Ir(MDQ)$_2$(acac) (1, 2, 6, and 8 wt %). [b] Voltages at 0.2 mA/cm^2. [c] Maximum efficiencies between 100 and 500 cd/m^2. [d] Commission International de l'Eclairage coordinates tested at 20 mA/cm^2. [e] The roll-off means efficiency roll-off from 500 to 5000 cd/m^2 in the OLEDs.

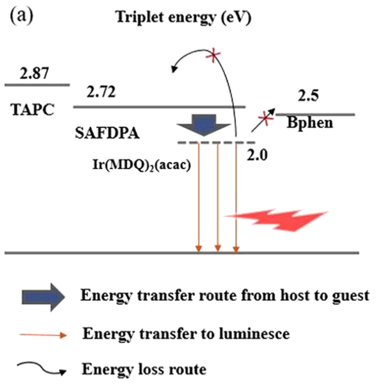


Figure 6. Triplet energy level Tl of TAPC, SAFDPA, BPhen, and Ir(MDQ)$_2$(acac) and energy transfer or loss routing of (a) the SAFDPA:host−guest luminescence system and (b) the exciplex:luminescence system.

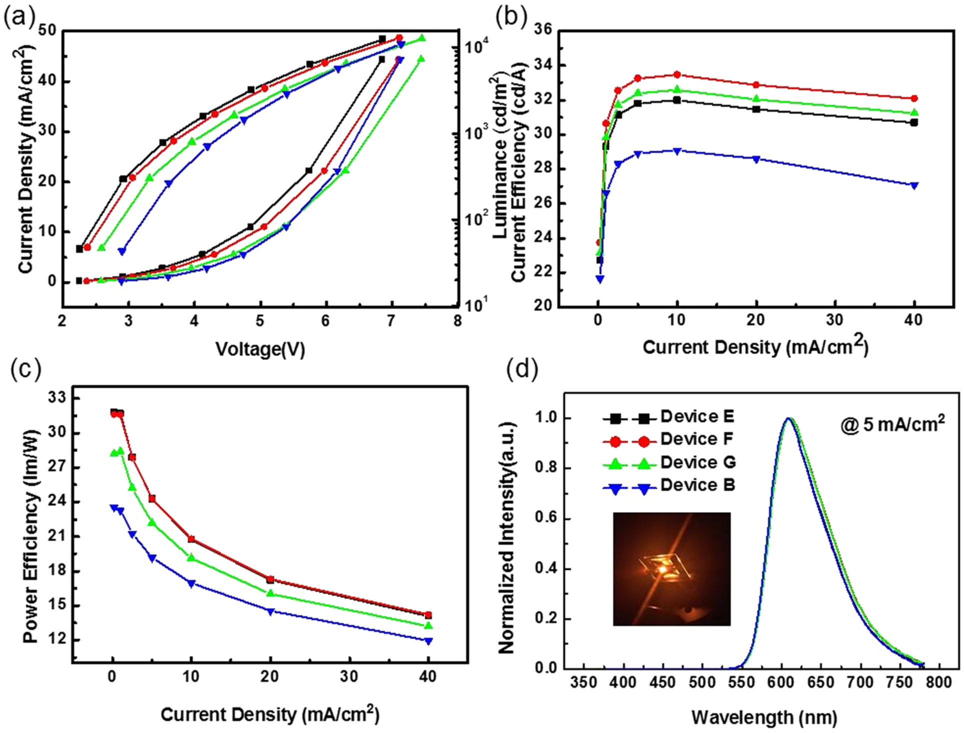


Figure 7. (a) Current density−voltage−luminance characteristics of devices. (b) Current efficiency−current density characteristics of devices. (c) Power efficiency−current density characteristics of devices. (d) Normalized EL spectra of devices.

changes with the decrease in doping proportion of Ir(MDQ)$_2$(acac) from 4 to 1%, while brightness increases to the peak value with 1% proportion of Ir(MDQ)$_2$(acac) before declining because of the strengthening of triplet−triplet annihilation, triplet−polaron quenching, and field-induced quenching with a higher proportion of dye. As exhibited in Figure 5b and c, a 2% doped rate of Ir(MDQ)$_2$(acac) reaches the maximum value of PE and CE in our optimized reference red PhOLEDs. The device properties of the reference PhOLEDs are summarized in Table 1, depicting the maximum CE and power efficiency (η_C, η_P) of 29.09 cd/A (EQE = 9.74%) and 23.54 lm/W, respectively, with light emission peaks of 608 nm. The CE roll-off of reference red PhOLEDs is low at 4.3% with 1% doping proportion.

DOI: 10.1021/acsami.6b13077
ACS Appl. Mater. Interfaces 2017, 9, 2701−2710

Table 2. EL Characteristics of the Designed Devices

device[a]	voltage[b] (V)	η_c[c] (cd/A)	η_p (lm/W)[c] (EQE)[c]	emission peak (nm)	CIE[d]	roll-off[e] (%), 500−5000 cd/m^2
E	2.24	32.00	31.80 (10.7%)	608	0.627, 0.372	3.47
F	2.36	32.87	31.60 (11.01%)	608	0.632, 0.368	1.41
G	2.57	32.58	28.18 (10.91%)	608	0.631, 0.368	1.41
B	2.88	29.09	23.54 (9.74%)	608	0.626, 0.372	4.28

[a] The devices E, F, and G have the same device structure with different thicknesses of SAFDPA (45, 35, and 25 nm), and B is the reference device. [b] Voltages at 0.2 mA/cm^2. [c] Maximum efficiencies between 100 and 500 cd/m^2. [d] Commission International de l'Eclairage coordinates measured at 20 mA/cm^2. [e] The roll-off means efficiency roll-off from 500 to 5000 cd/m^2 in the device.

In the perspective of hole transportation, as exhibited in Figure 2, there is a 0.2 eV barrier at the HAT-CN and TAPC interface and a 0.1 eV barrier at the interface between TAPC and SAFDPA along the HOMO level. Inserting an additional TAPC layer will separate the injection barrier of 0.3 eV between HAT-CN and SAFDPA into two smaller barriers, and thus enhance hole injection. However, the hole transport capacity of spiro-based materials[65] and lesser number of heterojunctions make up a little barrier introduced by removing TAPC. For the energy transfer process exhibited in Figure 6a, in the reference device, the 0.7 eV triplet state gap between the host (SAFDPA) and guest (Ir(MDQ)$_2$(acac)) primely confines the exciton energy to luminesce once the energy is successfully transferred to the energy state of Ir(MDQ)$_2$(acac). TAPC (T_1 = 2.87 eV) with a higher T_1 than the host material SAFDPA (T_1 = 2.72 eV) seems to be unnecessarily acting as an energy blocking layer. Therefore, as demonstrated in Figure 6b, in our highly simplified designed reddish orange PhOLEDs, without traditional hole-transport-material TAPC, we employ a novel spiro-exciplex-forming host which should show a lower triplet state than two mixed exciplex hosts SAFDPA and BPhen.[66] This lower exciplex triplet state offers a smooth energy transfer route to Ir(MDQ)$_2$(acac) and further lowers the energy of the luminescence system, compared with the host−guest luminescence system, which helps to achieve low CE roll-off of our designed PhOLEDs owing to enhanced efficiency and stability under high voltage. In order to confirm the proposed strategy, simplified designed reddish orange PhOLEDs have been fabricated and tested as follows.

Figure 7a shows a comparison of the J−V−L characteristics of the designed devices (E, F, G) with that of the reference device B. It can be seen that, at the same voltage, the spiro-exciplex-forming host reddish orange PhOLEDs show higher brightness and current than those of the conventional device with TAPC as the hole transport layer. For example, at a current density of 0.2 mA/cm^2, the driving voltages for B and F devices are 2.89 V (with a brightness of 43.3 cd/m^2) and 2.36 V (with a brightness of 47.5 cd/m^2), respectively. The lower driving voltage and higher brightness are attained by spiro-exciplex-forming host PhOLEDs. This can be mainly attributed to the superiority of the novel exciplex cohost at low driving voltage.[67] Moreover, the HOMO of SAFDPA matches primely with the energy level of HAT-CN/ITO, avoiding additional trap production by the extra interface of TAPC during the hole transporting process. Parts b and c of Figure 7 show the CE and PE with current density for designed device structures, respectively. Apparently, the EL characteristic spectra (Figure 7d) and CIE (Table 2), for both the spiro-exciplex-forming host incorporated PhOLEDs and reference device structures, are almost the same owing to the fact that the carrier recombination zone is primely limited within the emissive layer. Moreover, we optimized the device performance among devices E, F, and G. As the thickness of SAFDPA decreases from 45 to 25 nm, the PE and CE first increase, thanks to the equilibrium of the carrier injection with the 35 nm SAFDPA, and then decrease on account of thinner SAFDPA leading to imbalance of carrier injection and mismatch of optical field with an ultralow threshold voltage of 2.24 V, which revealed that novel spiro-based exciplex-forming hosts are useful in optimizing the carrier location and recombination zone, promoting the energy transfer from cohost to emitter because of their lower LUMO levels and suited triplet energies in simplified devices. As exhibited in Table 2, the peak current and power efficiencies (η_C, η_P) for the spiro-exciplex-forming host PhOLEDs are 32.87 cd/A (EQE = 11.01%) and 31.80 lm/W, respectively, whereas those for the reference device are 29.09 cd/A (EQE = 9.74%) and 23.54 lm/W, respectively, as exhibited in Figure 7. Particularly, the PE of the designed reddish orange PhOLEDs with exciplex-forming host enhance up to 36.2% mainly due to the lower operating voltage, compared with the reference device as exhibited in Figure 7. Due to the restrain of TTA in designed PhOLEDs by lower doping and exciplex host, their CE roll-off is as low as 1.41% within the brightness range from 500 to 5000 cd/m^2.

Spectral changes of all of the OLEDs with various current densities are studied by drawing the EL spectra by their corresponding current densities. Figure 8 shows the relative intensity EL spectra of the OLEDs using Ir(MDQ)$_2$(acac) as dopant with a proportion of 2 wt % at current densities of 0.2, 1, 20, and 40 mA/cm^2, respectively. The inset in Figure 8 exhibits the color shifts in the CIE 1931 chromaticity coordinates. The OLEDs show tiny changes in the CIE color

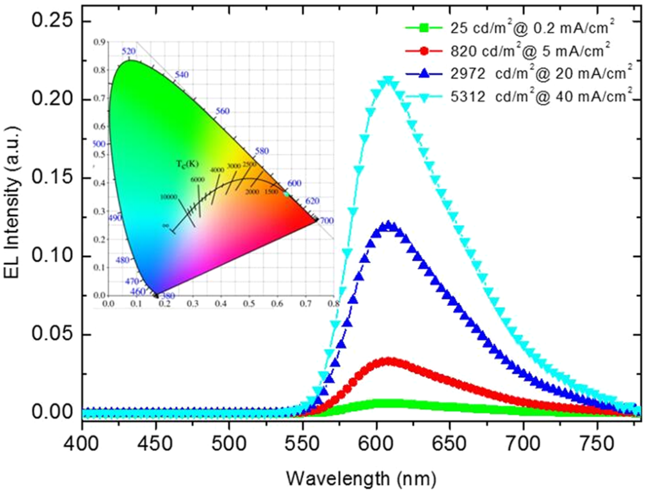


Figure 8. EL spectra of OLED E at various current densities of 0.2, 1, 20, and 40 mA/cm^2. The inset shows the CIE chromaticity coordinates of the OLEDs at various current densities.

coordinates with the mixed proportion of 2 wt % with the red dopant, changing from (0.628, 0.371) at 47.5 cd/m^2 to (0.627, 0.372) at 12836 cd/m^2. The peaks of the EL spectra of the devices are the same with stable CIE coordinates as the current density increases.

Figure 9 shows the operational lifetime of reddish orange PhOLED with spiro-exciplex-forming host and reference device. The lifetime or stability of the OLEDs were tested at the same initial brightness of 3000 cd/m^2 rather than general 500 cd/m^2 to accelerate the aging test. It is shown, compared with the reference OLED, the spiro-exciplex-forming host PhOLEDs show a longer operational lifetime, which mainly means less interfacial defects by removing an additional layer of TAPC, and in addition, the cohost helps to lower exciton accumulation which destroys the organic interface. Moreover, less homojunction helps to improve the device lifetime. T50 means the time to attain a 50% decay of luminescence;[68] T50 of the device improves from 10.7 to 14.1 h by applying a spiro-exciplex-forming host. Although this is not the key point needed to illustrate, lithium-ion doping can solve crystal of Bphen when the thickness of Bphen is more than 10 nm, helping to further lower the operating voltage and improve device lifetime.[69]

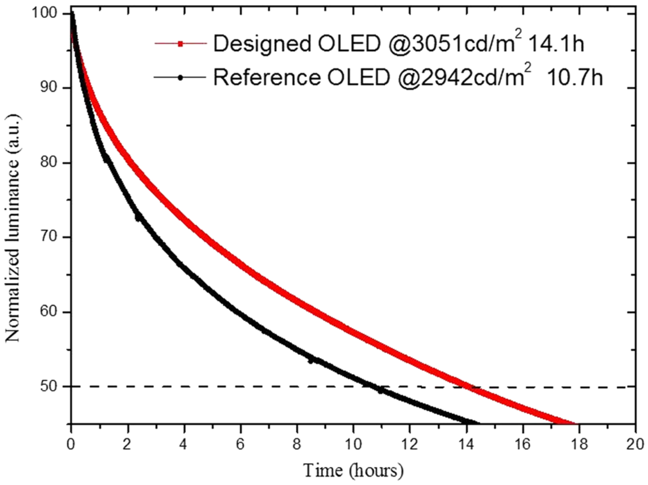


Figure 9. Normalized luminescence versus operational time of reference device A and designed device D, aging at the same brightness of 3000 cd/m^2 in order to accelerate the test. The OLEDs were simply packaged by cover glasses with adhesive coating in the atmosphere, and then tested in ambient air for lifetime evaluations.

4. CONCLUSIONS

In summary, highly simplified reddish orange PhOLEDs applying a novel spiro-exciplex-forming host with carrier- and exciton-confining function are successfully demonstrated, showing lower working voltage, better efficiency, and stability. Particularly, the power efficiency (PE) of designed reddish orange PhOLEDs with exciplex-forming cohost is enhanced up to 36.2%, compared with the reference device. The effective strategy to design highly simplified PhOLEDs by a spiro-exciplex-forming host has been verified and helps to simplify OLED structure, lower the cost, and popularize OLED technology.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b13077.

Experimental section; performance of reference OLEDs with SAFDPA:TmPyPB as the non-exciplex-forming cohost shown in Figure S1; the current density−voltage (*J*−*V*) curves for the hole-only devices showing charge transporting properties of the SAFDPA in Figure S2 (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (61575136, 51035008, 51373075) and National Basic Research Program of China (973 Program, 2015CB932200). This project was also funded by the Collaborative Innovation Center of Suzhou Nano Science and Technology, by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and by Shenzhen Key Laboratory of Organic Optoelectromagnetic Functional Materials of Shenzhen Science and Technology Plan (ZDSYS20140509094114164). This work was also financially supported by Shenzhen Science and Technology Research Grant (JCYJ20160510144254604), Guangdong Key Research Project (2014B090914003), the Shenzhen Peacock Plan (KQTD2014062714543296), Guangdong Academician Workstation (2013B090400016).

■ REFERENCES

(1) Shen, Z.; Burrows, P. E.; Bulović, V.; Forrest, S. R.; Thompson, M. E. Three-Color, Tunable, Organic Light-Emitting Devices. *Science* **1997**, *276* (5321), 2009−2011.

(2) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lussem, B.; Leo, K. White organic light-emitting diodes with fluorescent tube efficiency. *Nature* **2009**, *459* (7244), 234−238.

(3) Sun, Y.; Forrest, S. R. High-efficiency white organic light emitting devices with three separate phosphorescent emission layers. *Appl. Phys. Lett.* **2007**, *91* (26), 263503.

(4) Helander, M. G.; Wang, Z. B.; Qiu, J.; Greiner, M. T.; Puzzo, D. P.; Liu, Z. W.; Lu, Z. H. Chlorinated Indium Tin Oxide Electrodes with High Work Function for Organic Device Compatibility. *Science* **2011**, *332* (6032), 944−947.

(5) Ma, D. White OLED Devices. In *Handbook of Advanced Lighting Technology*; Karlicek, R., Sun, C.-C., Zissis, G., Ma, R., Eds.; Springer International Publishing: Cham, Switzerland, 2016; pp 1−34.

(6) Xu, T.; Yang, M.; Liu, J.; Wu, X.; Murtaza, I.; He, G.; Meng, H. Wide color-range tunable and low roll-off fluorescent organic light emitting devices based on double undoped ultrathin emitters. *Org. Electron.* **2016**, *37*, 93−99.

(7) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. Light-Emitting Polythiophenes. *Adv. Mater.* **2005**, *17* (19), 2281−2305.

(8) Luo, D. Y.; Yu, L. M.; Man, J. X.; Liu, T. L.; Li, J. J.; Xu, T.; Liu, Z.; Wang, Z. B.; Lu, Z. H. A bi-functional structure with tunable

electrical and optical properties for organic photovoltaic cells. *J. Appl. Phys.* **2013**, *113* (22), 224506.

(9) Mathews, S. Phytochrome-mediated development in land plants: red light sensing evolves to meet the challenges of changing light environments. *Mol. Ecol.* **2006**, *15* (12), 3483−3503.

(10) Elman, M.; Slatkine, M.; Harth, Y. The effective treatment of acne vulgaris by a high - intensity, narrow band 405−420 nm light source. *Journal of Cosmetic and Laser Therapy* **2003**, *5* (2), 111−117.

(11) Tao, Y.; Wang, Q.; Yang, C.; Wang, Q.; Zhang, Z.; Zou, T.; Qin, J.; Ma, D. A Simple Carbazole/Oxadiazole Hybrid Molecule: An Excellent Bipolar Host for Green and Red Phosphorescent OLEDs. *Angew. Chem.* **2008**, *120* (42), 8224−8227.

(12) Yen, F.-W.; Chiu, C.-Y.; Lin, I. F.; Teng, C.-M.; Lin, X.-H. P-183: Efficient Deep Blue, Blue, Green, Yellow, Reddish-Orange and Red Organic Light-Emitting Device using 2,7-Dipyrenespirofluorene (DPSF) as a Fluorescent Emitting Host. *Dig. Tech. Pap. - Soc. Inf. Disp. Int. Symp.* **2007**, *38* (1), 883−887.

(13) Tung, Y.-L.; Lee, S.-W.; Chi, Y.; Tao, Y.-T.; Chien, C.-H.; Cheng, Y.-M.; Chou, P.-T.; Peng, S.-M.; Liu, C.-S. Organic light-emitting diodes based on charge-neutral Os(ii) emitters: generation of saturated red emission with very high external quantum efficiency. *J. Mater. Chem.* **2005**, *15* (4), 460−464.

(14) Kwong, R. C.; Nugent, M. R.; Michalski, L.; Ngo, T.; Rajan, K.; Tung, Y.-J.; Weaver, M. S.; Zhou, T. X.; Hack, M.; Thompson, M. E.; Forrest, S. R.; Brown, J. J. High operational stability of electrophosphorescent devices. *Appl. Phys. Lett.* **2002**, *81* (1), 162−164.

(15) Watanabe, S.; Ide, N.; Kido, J. High-Efficiency Green Phosphorescent Organic Light-Emitting Devices with Chemically Doped Layers. *Jpn. J. Appl. Phys.* **2007**, *46* (3A), 1186.

(16) Jou, J.-H.; Shen, S.-M.; Chen, S.-H.; Wu, M.-H.; Wang, W.-B.; Wang, H.-C.; Lin, C.-R.; Chou, Y.-C.; Wu, P.-H.; Shyue, J.-J. Highly efficient orange-red phosphorescent organic light-emitting diode using 2,7-bis(carbazo-9-yl)-9,9-ditolyfluorene as the host. *Appl. Phys. Lett.* **2010**, *96* (14), 143306.

(17) Feng, Y.; Li, P.; Zhuang, X.; Ye, K.; Peng, T.; Liu, Y.; Wang, Y. A novel bipolar phosphorescent host for highly efficient deep-red OLEDs at a wide luminance range of 1000−10 000 cd m-2. *Chem. Commun.* **2015**, *51* (63), 12544−12547.

(18) Li, G.; Zhu, D.; Peng, T.; Liu, Y.; Wang, Y.; Bryce, M. R. Very High Efficiency Orange-Red Light-Emitting Devices with Low Roll-Off at High Luminance Based on an Ideal Host−Guest System Consisting of Two Novel Phosphorescent Iridium Complexes with Bipolar Transport. *Adv. Funct. Mater.* **2014**, *24* (47), 7420−7426.

(19) Huang, J.; Pfeiffer, M.; Werner, A.; Blochwitz, J.; Leo, K.; Liu, S. Low-voltage organic electroluminescent devices using pin structures. *Appl. Phys. Lett.* **2002**, *80* (1), 139−141.

(20) He, G.; Pfeiffer, M.; Leo, K.; Hofmann, M.; Birnstock, J.; Pudzich, R.; Salbeck, J. High-efficiency and low-voltage - i - n electrophosphorescent organic light-emitting diodes with double-emission layers. *Appl. Phys. Lett.* **2004**, *85* (17), 3911−3913.

(21) Gong, S.; Chang, Y.-L.; Wu, K.; White, R.; Lu, Z.-H.; Song, D.; Yang, C. High-Power-Efficiency Blue Electrophosphorescence Enabled by the Synergistic Combination of Phosphine-Oxide-Based Host and Electron-Transporting Materials. *Chem. Mater.* **2014**, *26* (3), 1463−1470.

(22) Su, S.-J.; Sasabe, H.; Pu, Y.-J.; Nakayama, K.-i.; Kido, J. Tuning Energy Levels of Electron-Transport Materials by Nitrogen Orientation for Electrophosphorescent Devices with an 'Ideal' Operating Voltage. *Adv. Mater.* **2010**, *22* (30), 3311−3316.

(23) Ye, H.; Chen, D.; Liu, M.; Su, S.-J.; Wang, Y.-F.; Lo, C.-C.; Lien, A.; Kido, J. Pyridine-Containing Electron-Transport Materials for Highly Efficient Blue Phosphorescent OLEDs with Ultralow Operating Voltage and Reduced Efficiency Roll-Off. *Adv. Funct. Mater.* **2014**, *24* (21), 3268−3275.

(24) Wang, J.; Chen, J.; Qiao, X.; Alshehri, S. M.; Ahamad, T.; Ma, D. Simple-Structured Phosphorescent Warm White Organic Light-Emitting Diodes with High Power Efficiency and Low Efficiency Roll-off. *ACS Appl. Mater. Interfaces* **2016**, *8* (16), 10093−10097.

(25) Wu, C.-H.; Shih, P.-I.; Shu, C.-F.; Chi, Y. Highly efficient red organic light-emitting devices based on a fluorene-triphenylamine host doped with an Os(II) phosphor. *Appl. Phys. Lett.* **2008**, *92* (23), 233303.

(26) Chien, C.-H.; Hsu, F.-M.; Shu, C.-F.; Chi, Y. Efficient red electrophosphorescence from a fluorene-based bipolar host material. *Org. Electron.* **2009**, *10* (5), 871−876.

(27) Jeon, W. S.; Park, T. J.; Kim, S. Y.; Pode, R.; Jang, J.; Kwon, J. H. Ideal host and guest system in phosphorescent OLEDs. *Org. Electron.* **2009**, *10* (2), 240−246.

(28) Zhou, L.; Li, L.; Jiang, Y.; Cui, R.; Li, Y.; Zhao, X.; Zhang, H. Rare Earth Complex as Electron Trapper and Energy Transfer Ladder for Efficient Red Iridium Complex Based Electroluminescent Devices. *ACS Appl. Mater. Interfaces* **2015**, *7* (29), 16046−16053.

(29) Li, Y.; Zhou, L.; Cui, R.; Jiang, Y.; Zhao, X.; Liu, W.; Zhu, Q.; Cui, Y.; Zhang, H. High performance red organic electroluminescent devices based on a trivalent iridium complex with stepwise energy levels. *RSC Adv.* **2016**, *6* (75), 71282−71286.

(30) Su, S.-J.; Gonmori, E.; Sasabe, H.; Kido, J. Highly Efficient Organic Blue-and White-Light-Emitting Devices Having a Carrier- and Exciton-Confining Structure for Reduced Efficiency Roll-Off. *Adv. Mater.* **2008**, *20* (21), 4189−4194.

(31) Li, X.-L.; Ouyang, X.; Liu, M.; Ge, Z.; Peng, J.; Cao, Y.; Su, S.-J. Highly efficient single- and multi-emission-layer fluorescent/phosphorescent hybrid white organic light-emitting diodes with [similar]20% external quantum efficiency. *J. Mater. Chem. C* **2015**, *3* (35), 9233−9239.

(32) Sun, J. W.; Kim, K.-H.; Moon, C.-K.; Lee, J.-H.; Kim, J.-J. Highly Efficient Sky-Blue Fluorescent Organic Light Emitting Diode Based on Mixed Cohost System for Thermally Activated Delayed Fluorescence Emitter (2CzPN). *ACS Appl. Mater. Interfaces* **2016**, *8* (15), 9806−9810.

(33) Hung, W.-Y.; Chiang, P.-Y.; Lin, S.-W.; Tang, W.-C.; Chen, Y.-T.; Liu, S.-H.; Chou, P.-T.; Hung, Y.-T.; Wong, K.-T. Balance the Carrier Mobility To Achieve High Performance Exciplex OLED Using a Triazine-Based Acceptor. *ACS Appl. Mater. Interfaces* **2016**, *8* (7), 4811−4818.

(34) Zhang, Y.; Aziz, H. Influence of the Guest on Aggregation of the Host by Exciton−Polaron Interactions and Its Effects on the Stability of Phosphorescent Organic Light-Emitting Devices. *ACS Appl. Mater. Interfaces* **2016**, *8* (22), 14088−14095.

(35) Choong, V.-E.; Shi, S.; Curless, J.; Shieh, C.-L.; Lee, H.-C.; So, F.; Shen, J.; Yang, J. Organic light-emitting diodes with a bipolar transport layer. *Appl. Phys. Lett.* **1999**, *75* (2), 172−174.

(36) Aziz, H.; Popovic, Z. D.; Hu, N.-X.; Hor, A.-M.; Xu, G. Degradation Mechanism of Small Molecule-Based Organic Light-Emitting Devices. *Science* **1999**, *283* (5409), 1900−1902.

(37) Seino, Y.; Inomata, S.; Sasabe, H.; Pu, Y.-J.; Kido, J. High-Performance Green OLEDs Using Thermally Activated Delayed Fluorescence with a Power Efficiency of over 100 lm W−1. *Adv. Mater.* **2016**, *28* (13), 2638−2643.

(38) Lee, J.-H.; Ho, Y.-H.; Lin, T.-C.; Wu, C.-F. High-Efficiency Fluorescent Blue Organic Light-Emitting Device with Balanced Carrier Transport. *J. Electrochem. Soc.* **2007**, *154* (7), J226−J228.

(39) Nasu, K.; Nakagawa, T.; Nomura, H.; Lin, C.-J.; Cheng, C.-H.; Tseng, M.-R.; Yasuda, T.; Adachi, C. A highly luminescent spiro-anthracenone-based organic light-emitting diode exhibiting thermally activated delayed fluorescence. *Chem. Commun.* **2013**, *49* (88), 10385−10387.

(40) Méhes, G.; Nomura, H.; Zhang, Q.; Nakagawa, T.; Adachi, C. Enhanced Electroluminescence Efficiency in a Spiro-Acridine Derivative through Thermally Activated Delayed Fluorescence. *Angew. Chem., Int. Ed.* **2012**, *51* (45), 11311−11315.

(41) Ganesan, P.; Fu, K.; Gao, P.; Raabe, I.; Schenk, K.; Scopelliti, R.; Luo, J.; Wong, L. H.; Gratzel, M.; Nazeeruddin, M. K. A simple spiro-type hole transporting material for efficient perovskite solar cells. *Energy Environ. Sci.* **2015**, *8* (7), 1986−1991.

(42) Hu, Z.; Fu, W.; Yan, L.; Miao, J.; Yu, H.; He, Y.; Goto, O.; Meng, H.; Chen, H.; Huang, W. Effects of heteroatom substitution in

spiro-bifluorene hole transport materials. *Chemical Science* **2016**, 7 (8), 5007−5012.

(43) Xu, T.; Yan, L.; Miao, J.; Hu, Z.; Shao, S.; Li, A.; Murtaza, I.; Meng, H. Unlocking the potential of diketopyrrolopyrrole-based solar cells by a pre-solvent annealing method in all-solution processing. *RSC Adv.* **2016**, *6* (58), 53587−53595.

(44) Baldo, M. A.; Adachi, C.; Forrest, S. R. Transient analysis of organic electrophosphorescence. II. Transient analysis of triplet-triplet annihilation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62* (16), 10967−10977.

(45) Reineke, S.; Walzer, K.; Leo, K. Triplet-exciton quenching in organic phosphorescent light-emitting diodes with Ir-based emitters. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75* (12), 125328.

(46) Zhang, Y.-X.; Zhang, L.; Cui, L.-S.; Gao, C.-H.; Chen, H.; Li, Q.; Jiang, Z.-Q.; Liao, L.-S. Control of Conjugation Degree via Position Engineering to Highly Efficient Phosphorescent Host Materials. *Org. Lett.* **2014**, *16* (14), 3748−3751.

(47) Chopra, N.; Swensen, J. S.; Polikarpov, E.; Cosimbescu, L.; So, F.; Padmaperuma, A. B. High efficiency and low roll-off blue phosphorescent organic light-emitting devices using mixed host architecture. *Appl. Phys. Lett.* **2010**, *97* (3), 033304.

(48) Zhang, L.; Zu, F.-S.; Deng, Y.-L.; Igbari, F.; Wang, Z.-K.; Liao, L.-S. Origin of Enhanced Hole Injection in Organic Light-Emitting Diodes with an Electron-Acceptor Doping Layer: p-Type Doping or Interfacial Diffusion? *ACS Appl. Mater. Interfaces* **2015**, *7* (22), 11965−11971.

(49) Tang, X.; Qian, M.; Zhou, D.-Y.; Ding, L.; Hu, Y.; Liao, L.-S. A surface modification layer capable of tolerating substrate contamination on transparent electrodes of organic electronic devices. *Org. Electron.* **2016**, *28*, 217−224.

(50) Lai, S.-L.; Tong, Q.-X.; Chan, M.-Y.; Ng, T.-W.; Lo, M.-F.; Lee, S.-T.; Lee, C.-S. Distinct electroluminescent properties of triphenylamine derivatives in blue organic light-emitting devices. *J. Mater. Chem.* **2011**, *21* (4), 1206−1211.

(51) Mikie, T.; Saeki, A.; Masuda, H.; Ikuma, N.; Kokubo, K.; Seki, S. New efficient (thio)acetalized fullerene monoadducts for organic solar cells: characterization based on solubility, mobility balance, and dark current. *J. Mater. Chem. A* **2015**, *3* (3), 1152−1157.

(52) Wang, Y.-K.; Yuan, Z.-C.; Shi, G.-Z.; Li, Y.-X.; Li, Q.; Hui, F.; Sun, B.-Q.; Jiang, Z.-Q.; Liao, L.-S. Dopant-Free Spiro-Triphenylamine/Fluorene as Hole-Transporting Material for Perovskite Solar Cells with Enhanced Efficiency and Stability. *Adv. Funct. Mater.* **2016**, *26* (9), 1375−1381.

(53) Earmme, T.; Jenekhe, S. A. High-performance multilayered phosphorescent OLEDs by solution-processed commercial electron-transport materials. *J. Mater. Chem.* **2012**, *22* (11), 4660−4668.

(54) Su, S.-J.; Chiba, T.; Takeda, T.; Kido, J. Pyridine-Containing Triphenylbenzene Derivatives with High Electron Mobility for Highly Efficient Phosphorescent OLEDs. *Adv. Mater.* **2008**, *20* (11), 2125−2130.

(55) Hung, W.-Y.; Ke, T.-H.; Lin, Y.-T.; Wu, C.-C.; Hung, T.-H.; Chao, T.-C.; Wong, K.-T.; Wu, C.-I. Employing ambipolar oligofluorene as the charge-generation layer in time-of-flight mobility measurements of organic thin films. *Appl. Phys. Lett.* **2006**, *88* (6), 064102.

(56) Wu, I. W.; Wang, P.-S.; Tseng, W.-H.; Chang, J.-H.; Wu, C.-I. Correlations of impedance−voltage characteristics and carrier mobility in organic light emitting diodes. *Org. Electron.* **2012**, *13* (1), 13−17.

(57) Borsenberger, P. M. The concentration dependence of the hole mobility of 1,1 - bis(di - 4 - tolylaminophenyl)cyclohexane doped bisphenol - A - olycarbonate. *J. Appl. Phys.* **1992**, *72* (11), 5283−5287.

(58) Miśnik, M.; Falkowski, K.; Mróz, W.; Stampor, W. Electromodulation of photoluminescence in vacuum-evaporated films of bathocuproine. *Chem. Phys.* **2013**, *410*, 45−54.

(59) Zhang, T.; Chu, B.; Li, W.; Su, Z.; Peng, Q. M.; Zhao, B.; Luo, Y.; Jin, F.; Yan, X.; Gao, Y.; Wu, H.; Zhang, F.; Fan, D.; Wang, J. Efficient Triplet Application in Exciplex Delayed-Fluorescence OLEDs Using a Reverse Intersystem Crossing Mechanism Based on a ΔES−T of around Zero. *ACS Appl. Mater. Interfaces* **2014**, *6* (15), 11907−11914.

(60) Cherpak, V.; Stakhira, P.; Minaev, B.; Baryshnikov, G.; Stromylo, E.; Helzhynskyy, I.; Chapran, M.; Volyniuk, D.; Hotra, Z.; Dabuliene, A.; Tomkeviciene, A.; Voznyak, L.; Grazulevicius, J. V. Mixing of Phosphorescent and Exciplex Emission in Efficient Organic Electroluminescent Devices. *ACS Appl. Mater. Interfaces* **2015**, *7* (2), 1219−1225.

(61) Michaleviciute, A.; Gurskyte, E.; Volyniuk, D. Y.; Cherpak, V. V.; Sini, G.; Stakhira, P. Y.; Grazulevicius, J. V. Star-Shaped Carbazole Derivatives for Bilayer White Organic Light-Emitting Diodes Combining Emission from Both Excitons and Exciplexes. *J. Phys. Chem. C* **2012**, *116* (39), 20769−20778.

(62) Park, Y.-S.; Kim, K.-H.; Kim, J.-J. Efficient triplet harvesting by fluorescent molecules through exciplexes for high efficiency organic light-emitting diodes. *Appl. Phys. Lett.* **2013**, *102* (15), 153306.

(63) Duan, J. P.; Sun, P. P.; Cheng, C. H. New Iridium Complexes as Highly Efficient Orange−Red Emitters in Organic Light-Emitting Diodes. *Adv. Mater.* **2003**, *15* (3), 224−228.

(64) Xiang, C.; Koo, W.; So, F.; Sasabe, H.; Kido, J. A systematic study on efficiency enhancements in phosphorescent green, red and blue microcavity organic light emitting devices. *Light: Sci. Appl.* **2013**, *2*, e74.

(65) Xue, M.-M.; Huang, C.-C.; Yuan, Y.; Cui, L.-S.; Li, Y.-X.; Wang, B.; Jiang, Z.-Q.; Fung, M.-K.; Liao, L.-S. De Novo Design of Boron-Based Host Materials for Highly Efficient Blue and White Phosphorescent OLEDs with Low Efficiency Roll-Off. *ACS Appl. Mater. Interfaces* **2016**, *8* (31), 20230−20236.

(66) Seino, Y.; Sasabe, H.; Pu, Y.-J.; Kido, J. High-Performance Blue Phosphorescent OLEDs Using Energy Transfer from Exciplex. *Adv. Mater.* **2014**, *26* (10), 1612−1616.

(67) Lee, J.-H.; Cheng, S.-H.; Yoo, S.-J.; Shin, H.; Chang, J.-H.; Wu, C.-I.; Wong, K.-T.; Kim, J.-J. An Exciplex Forming Host for Highly Efficient Blue Organic Light Emitting Diodes with Low Driving Voltage. *Adv. Funct. Mater.* **2015**, *25* (3), 361−366.

(68) Tyan, Y.-S. Organic light-emitting-diode lighting overview. *J. Photonics Energy* **2011**, *1* (1), 011009−011009−15.

(69) Kondakov, D. Y. Voltammetric study of Bphen electron-transport layer in contact with LiF/Al cathode in organic light-emitting diodes. *J. Appl. Phys.* **2006**, *99* (2), 024901.