ACS APPLIED MATERIALS & INTERFACES
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Above 30% External Quantum Efficiency in Green Delayed Fluorescent Organic Light-Emitting Diodes

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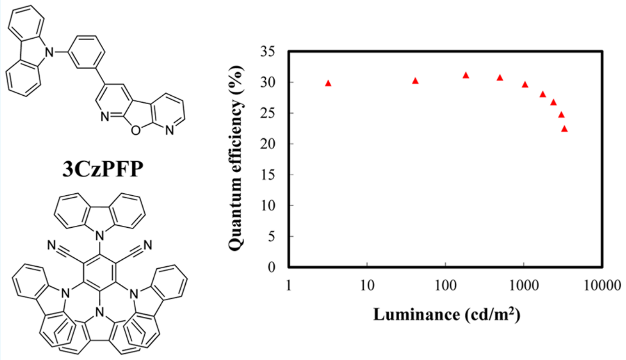
Ⓢ *Supporting Information*

ABSTRACT: Highly efficient green thermally activated delayed fluorescent organic light-emitting diodes with an external quantum efficiency of 31.2% were investigated by using 3-(3-(carbazole-9-yl)phenyl) pyrido[3′,2′:4,5]furo[2,3-*b*]pyridine (3CzPFP) derived from carbazole and pyrido[3′,2′:4,5]furo-[2,3-*b*]pyridine. The host material showed well-matched photoluminescence emission with absorption of the green dopant material, (4s,6s)-2,4,5,6-tetra(9*H*-carbazol-9-yl)-isophthalonitrile (4CzIPN) and harvested all excitons of 4CzIPN. The 3CzPFP:4CzIPN film exhibited high photoluminescence quantum yield of 100%, and the green delayed fluorescence device employing the 3CzPFP host showed high maximum quantum efficiency of 31.2 ± 0.5% at 1% doping after optimization of the device structure.



KEYWORDS: *green fluorescent device, bipolar host, high quantum efficiency, high triplet energy, delayed fluorescence*

■ INTRODUCTION

External quantum efficiency is a key characteristic of organic light-emitting diodes (OLEDs) and much effort has been devoted to boost the efficiency. It is important to harvest all excitons to achieve 100% internal quantum efficiency in OLEDs and phosphorescent OLEDs can utilize all excitons because of strong spin−orbit coupling of triplet emitters.[1] The spin−orbit coupling of triplet emitters enabled the light emission of triplet excitons by allowing forbidden transition between triplet state and singlet state. Therefore, phosphorescent OLEDs can reach internal quantum efficiency of 100% as demonstrated in several works.[2,3]

In addition to the phosphorescence, the use of delayed fluorescence has been explored as an approach to utilize all excitons.[4−14] In this case, intersystem crossing between triplet and singlet states was activated without any heavy metal, yielding high-efficiency OLEDs. It has been known that *p*-type delayed fluorescence, which takes advantage of triplet−triplet annihilation, can convert triplet excitons into singlet excitons, but theoretical efficiency is limited to 62.5% due to triplet fusion.[4,5] However, the delayed fluorescence via triplet−triplet annihilation was not effective, and no work has reported above 62.5% internal quantum efficiency in triplet fusion type fluorescent OLEDs.

Another delayed fluorescence for both singlet and triplet harvesting is thermally activated delayed fluorescence (TADF) which uses all excitons by singlet−triplet mixing via small singlet−triplet exciton energy gap.[6−14] In the case of TADF mechanism, all excitons can exist as singlet excitons, which can give rise to radiative transition to ground state. After Adachi et al. reported 19.3% external quantum efficiency using a green TADF emitting material, (4s,6s)-2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN),[6] the efficiency was improved 29.6% by engineering host materials.[15−17] However, the quantum efficiency of 29.6% was obtained only when mixed host structure was used as published in phosphorescent emitter based green OLEDs.[2,18] The best quantum efficiency achieved in a single host device was 26.7%.[17] Therefore, the host materials for optimized TADF emission are essential to further boost the external quantum efficiency.

In this work, high-efficiency green TADF OLEDs were devised, taking advantage of a bipolar host material, 3-(3-(carbazole-9-yl)phenyl) pyrido[3′,2′:4,5]furo[2,3-*b*]pyridine (3CzPFP), by doping the 4CzIPN emitter. The main achievement made in this work using the 3CzPFP host was a high quantum efficiency of 31.2% in addition to little efficiency reduction at high luminance and device optimization at 1% doping.

Received: February 7, 2015
Accepted: April 21, 2015
Published: April 29, 2015

DOI: 10.1021/acsami.5b01220
ACS Appl. Mater. Interfaces 2015, 7, 9625−9629

■ EXPERIMENTAL SECTION

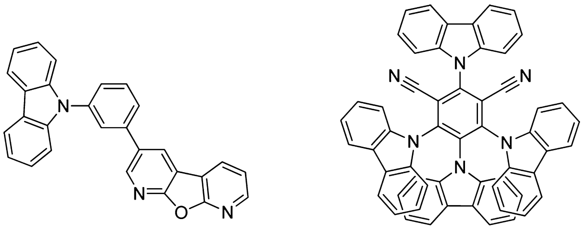
Device Fabrication and Measurements. TADF OLEDs were prepared by stacking organic layers on indium tin oxide (ITO) substrate using film coating process. Device stack structure and fabrication process was the same as that reported in our early work.[19] The only difference was the host material. 3CzPFP was already reported and was prepared according to the synthetic method reported earlier.[20] Encapsulation of the TADF OLEDs was performed by sealing the TADF OLEDs with a glass lid using an epoxy type UV curable sealant. Detailed device measurement was also described in other work.[19]

■ RESULTS AND DISCUSSION

Complete singlet and triplet exciton harvesting and unity charge balance factor are compulsory to reach the maximum device efficiency in TADF OLEDs. Therefore, the host materials should have high emission energy, appropriate PL emission, bipolar carrier transporting character, and energy levels for good charge injection. Other than these requirements, one additional condition is no exciplex formation between host and TADF dopant.[19] We reported 3-(furo[2,3-b:5,4-b′]-dipyridin-3-yl)-*N*,*N*-diphenylaniline (3TPAPFP) in the emitting layer doped with 4CzIPN.[19] Although high efficiency was attained in the 4CzIPN doped 3CzPFP device, exciplex generated from 3TPAPFP and 4CzIPN limited full utilization of the light emitting ability of the 4CzIPN device. Therefore, host materials without exciplex formation is more suitable for 4CzIPN and main approach taken in the present work was to choose and apply exciplex free host having the merit of bipolar charge transport character observed in previous 3TPAPFP host. The replacement of diphenylamine of 3TPAPFP with carbazole of 3CzPFP which, using the same electron transport unit, may solve the problem of exciplex formation of the 3TPAPFP:4CzIPN emitting system and enhance the device efficiency of 4CzIPN devices.

In previous research, the 3CzPFP was synthesized as green phosphorescent OLEDs host material.[20] The 3CzPFP has a molecular structure possessing electron rich 9-phenylcarbazole and electron poor pyrido[3′,2′:4,5]furo[2,3-*b*]pyridine (PFP). The two moieties were connected through *meta*- position to manage the emission energy. As the high triplet energy 9-phenylcarbazole and PFP moieties were included as building blocks, the 3CzPFP host can show emission energy high enough to transfer to 4CzIPN. The photoluminescence (PL) emission of 3CzPFP can also be overlapped with the ultraviolet−visible (UV−vis) absorption (∼480 nm) of the 4CzIPN dopant because the conjugation of the molecules was not greatly extended. In addition, the carbazole and PFP moieties of the 3CzPFP host material enable separate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) manipulation for suppressed exciton quenching and similar hole and electron carrier density in the device.[21] In particular, the carbazole unit of 3CzPFP may not generate exciplex between 3CzPFP and 4CzIPN by weak electron donating character of 3CzPFP, Synthesis of 3CzPFP was described in our previous work.[20] The chemical structures of 3CzPFP and 4CzIPN are shown in Figure 1.

Photophysical absorption and emission of host and dopant were analyzed to study the overlap of the PL emission of 3CzPFP with UV−vis absorption of 4CzIPN. UV−vis spectrum of 4CzIPN in addition to PL emission spectrum of 3CzPFP are presented in Figure 2. Solid PL emission of 3CzPFP at 412 nm and UV−vis absorption of 4CzIPN below 480 nm were overlapped each other, implying good energy transfer between 3CzPFP and 4CzIPN. Triplet energy of the 3CzPFP host was 2.82 eV.[20]



3CzPFP **4CzIPN**

Figure 1. Chemical structures of 3CzPFP and 4CzIPN.

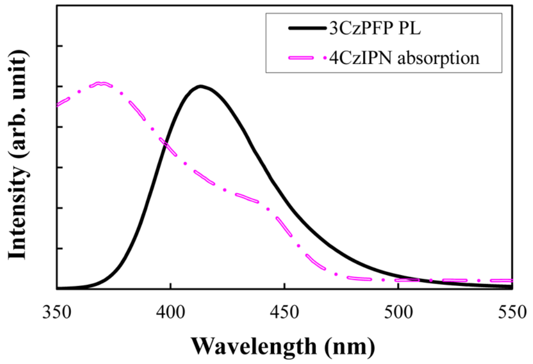


Figure 2. UV−vis absorption spectrum of 4CzIPN and PL emission spectrum of 3CzPFP.

PL quantum yield of the 3CzPFP:4CzIPN film was analyzed by absolute PL measurement using integrating sphere. PL quantum efficiency of the 3CzPFP:4CzIPN films was measured at different 4CzIPN doping concentration. 3CzPFP:4CzIPN showed PL quantum yield of 100% at 1% doping and it was reduced at high doping by concentration quenching effect. PL quantum efficiencies at 3 and 5% doping concentrations were 98 ± 2 and 96 ± 2%, respectively (Figure S2, Supporting Information).

The TADF process of the 3CzPFP:4CzIPN film was studied by transient PL measurements. Figure 3 represents transient PL spectra of 3CzPFP:4CzIPN film at temperature range from 60 K to room temperature. Prompt fluorescent emission at a short

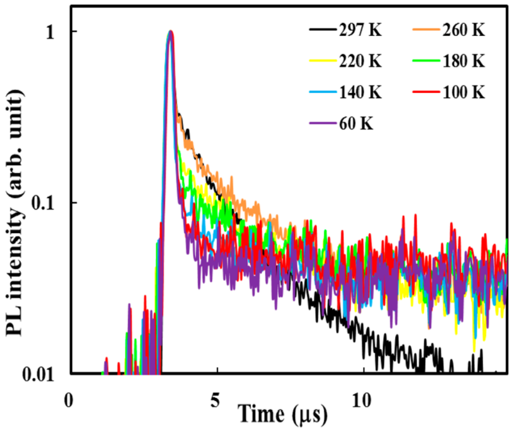


Figure 3. Transient PL spectra of 4CzIPN doped 3CzPFP film at different temperatures.

time scale less than 1 μs and delayed fluorescent emission after the prompt fluorescence were observed in the transient PL measurement. The delayed emission was very weak at low temperature below 100 K, but it was intensified at high temperature by thermal activation process of the delayed emission, which suggests that the origin of the delayed emission is TADF rather than triplet−triplet fusion. The rather fast transient PL decay at room temperature is caused by efficient thermal activation of reverse intersystem crossing process.

As the 3CzPFP host activated the delayed emission of 4CzIPN, green TADF devices were prepared by codeposition of 3CzPFP host with 4CzIPN. 4CzIPN concentration was varied from 0.5 to 3.0%. Current density−voltage and luminance−voltage relationship of the 3CzPFP:4CzIPN device are described in Figure 4. Similar current density and luminance were detected at all doping concentrations. As the 3CzPFP host had the narrow bandgap of 3.02 eV and the HOMO/LUMO level of −6.08/−3.06 eV from cyclic voltammetry measurement (Figure S1, Supporting Information; LUMO was calculated from HOMO and UV−vis edge in previous work[20]), charges are easily injected into the 3CzPFP host and energy transfer mainly contributes to the emission process. Therefore, charge trapping is not significant, and 4CzIPN doping concentration did not affect the current density.

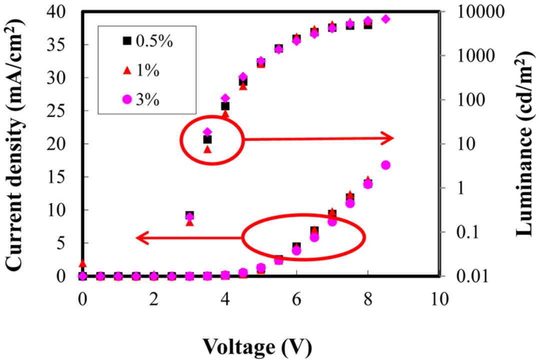


Figure 4. Current density−voltage-luminance curves of 3CzPFP devices doped with 4CzIPN according to 4CzIPN doping concentration.

Quantum efficiency of the 3CzPFP:4CzIPN devices are presented in Figure 5 according to luminance. Optimum doping concentration was 1% and optimized quantum efficiency was 28.7% in the 3CzPFP:4CzIPN device. Compared with the device data reported by Adachi et al. using the same 4CzIPN dopant,[6] 50% enhancement of quantum efficiency was observed and the optimum doping concentration was reduced from 5 to 1% by using 3CzPFP as the host material. The enhanced device efficiency of the 3CzPFP:4CzIPN device results from the contribution of high PL quantum yield of the 3CzPFP:4CzIPN film, bipolar charge transport properties of 3CzPFP,[20] and efficient TADF emission of 4CzIPN without any exciplex formation. Both hole and electron transport character of 3CzPFP allowed charge balance, and the balanced charge density increased the device efficiency of the 3CzPFP:4CzIPN devices. The TADF activation by the 3CzPFP host as confirmed by transient PL measurements also enhanced the device efficiency of the 3CzPFP devices. Particularly, exciplex was not formed between 3CzPFP and 4CzIPN, as can be proved by the emission spectra in Figure 7, which improved the quantum efficiency compared with 3TPAPFP host.[19] In addition, charge and exciton confinement by the hole and electron transport materials improved recombination efficiency due to energy barriers of 0.69 and 0.66 eV for hole and electron leakage, respectively (Figure 6). Triplet exciton quenching was also suppressed by high triplet energy of carrier transport layers.

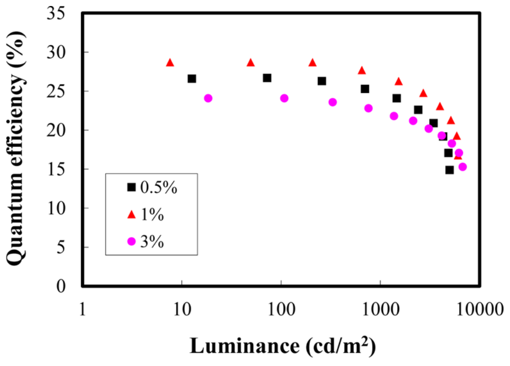


Figure 5. Quantum efficiency−luminance curves 3CzPFP devices doped with 4CzIPN according to 4CzIPN doping concentration.

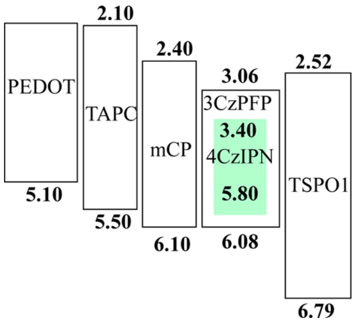


Figure 6. Energy level diagram of 3CzPFP device.

The low optimum doping concentration of 1% of the 3CzPFP device is related with high PL quantum efficiency at low doping and emission process dominated by energy transfer. PL quantum efficiency of 3CzPFP:4CzIPN was 100% at 1% doping concentration as explained in PL quantum efficiency data and concentration quenching effect decreased the quantum yield at high doping concentration. Additionally, the 0 eV energy barrier for charge injection between carrier transport layers and the 3CzPFP host makes energy transfer dominate emission process. Therefore, 1% optimum doping concentration was realized in the 3CzPFP:4CzIPN device. The rather large efficiency reduction at high luminance is due to instability of charge transport materials and low electron mobility of electron transport material.

Light emission of the 3CzPFP:4CzIPN devices is displayed in Figure 7. Electroluminescent emission of 4CzIPN was observed with no emission from the 3CzPFP host material. Color coordinate of 3CzPFP device at 1% doping concentration was (0.23,0.51).

The thickness of the electron transport layer was optimized to further improve the device efficiency based on the optical simulation results. Figure 8 shows measured quantum efficiency compared with calculated quantum efficiency data according to the thickness of the electron transport layer of the 3CzPFP:4CzIPN devices. Optimum thickness of the device was 40 nm, and high maximum quantum efficiency of 31.2 ±

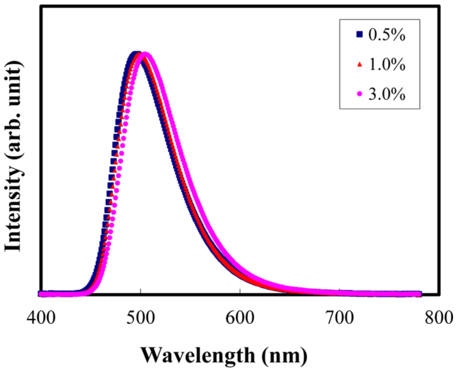


Figure 7. Electroluminescence spectra of 3CzPFP devices doped with 4CzIPN.

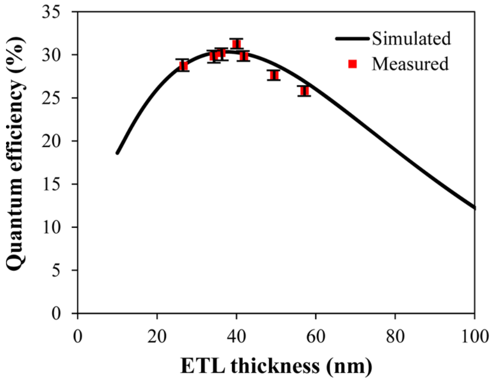


Figure 8. Simulated and measured external quantum efficiency of the 3CzPFP devices according to the thickness of the electron transport layer.

0.5% was obtained, which agreed with the optical simulation data of the device using an optical model based on dipole model.[22] Both singlet and triplet harvesting without electrical loss was assumed, and optical parameters measured for each organic layer was used for the calculation. The quantum efficiency at 1000 cd/m^2 was 29.7%. Considering that the best quantum efficiency of green phosphorescent OLEDs was 30.2%,[15] and the best efficiency of green TADF OLEDs fabricated utilizing a single host was 26.7%,[17] the quantum efficiency demonstrated in this work is better than any other data reported in green devices. Although Adachi et al. proposed comparable TADF device efficiency to phosphorescent device efficiency, the device efficiency of the TADF devices was much lower than that of phosphorescent devices. However, we proved that both TADF OLEDs and phosphorescent OLEDs are similar in terms of quantum efficiency. Complete activation of singlet and triplet excitons followed by efficient fluorescence emission was first demonstrated in this work using 3CzPFP. Quantum efficiency−luminance plots of the 3CzPFP device with 40 nm thick electron transport layer are presented in Figure 9. However, the lifetime of the 3CzPFP:4CzIPN device was poor and further device work and material development is necessary.

■ CONCLUSIONS

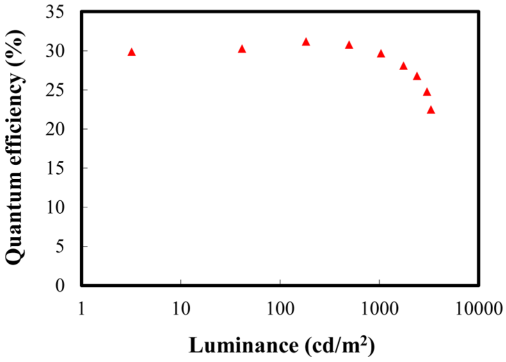


Figure 9. Quantum efficiency−luminance curve of the 3CzPFP device with 40 nm thick TSPO1 layer.

In conclusion, high quantum efficiency of 31.2 ± 0.5% could be realized in the 4CzIPN TADF device by taking advantage of 3CzPFP as the host material for 4CzIPN at a low doping concentration of 1% due to bipolar charge transport character, high PL quantum yield of 100%, and complete exciton harvesting. The TADF OLEDs was found to have an efficiency comparable to that of phosphorescent OLEDs, and the TADF devices are promising as high-efficiency OLEDs to improve the power consumption.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional cyclic voltammetry data and PL quantum yields. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (2013R1A1A2007991) and the Ministry of Science, ICT, and future Planning (2013R1A2A2A01067447).

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