Design Rule of Assistant Dopant for High External Quantum Efficiency in Hyperfluorescence Organic Light-Emitting Diodes

Ji Seon Jang, Si Hyun Han, and JunYeob Lee*

The design rule of an assistant dopant for enhanced external quantum efficiency (EQE) in hyperfluorescence organic light-emitting diodes is investigated by synthesizing two assistant dopants with thermally activated delayed fluorescent (TADF) features, BPAc and BPAcCz, by combining a benzophenone acceptor and a dimethylacridane donor. BPAc has only the benzophenone acceptor and the dimethylacridane donor, whereas BPAcCz has an extra carbazole donor added to the BPAc structure. Comparison of the two assistant dopants reveals that the incorporation of the donor unit with a small dihedral angle degrades the efficiency of the hyperfluorescence devices by Dexter energy transfer. The hyperfluorescence devices with the BPAc and BPAcCz assistant dopants exhibit EQE of 16.6% and 15.0%, respectively.

1. Introduction

The pursuit of high external quantum efficiency (EQE) in fluorescent organic light-emitting diodes (OLEDs) has long been a challenging issue because the EQE of common fluorescent OLEDs is limited to 5% assuming that only singlet excitons can contribute to the fluorescence. The ratio of singlet excitons to the triplet excitons in the electroluminescence (EL) process is only 25% and the conversion of the singlet excitons into photons may result in only 5% EQE, assuming an outcoupling efficiency of OLEDs of 20%. However, an EQE of 5% is too low compared with 20% of phosphorescent OLEDs, which has led to intensive research targeted at enhancing the EQE of fluorescent OLEDs.

Two mechanisms are available to increase the EQE of the fluorescent OLEDs. One is to transform triplet excitons into singlet excitons by upconversion process triggered by thermal activation. This process is called thermally activated delayed fluorescence (TADF) and the internal quantum efficiency can be 100% when all triplet excitons are converted into singlet excitons. Many TADF emitters showing close to 100% exciton conversion efficiency were reported. The other mechanism is to derive fluorescence without any electrogenerated excitons in the fluorescent emitter. In the electrogeneration process, both singlet and triplet excitons are formed in the fluorescent emitter and the ratio of singlet excitons is only 25%. However, the ratio of singlet excitons can be 100% when excitons are generated in the fluorescent emitter by only Förster energy transfer process. This process, called hyperfluorescence, was demonstrated by adding an assistant dopant capable of harvesting all excitons for light emission. In the hyperfluorescence mechanism, TADF materials are the assistant dopant and the fluorescent emitter emits by the Förster energy transfer mechanism. Therefore, the TADF material acting as an assistant dopant is critical to the EQE of the hyperfluorescent OLEDs. Several assistant dopant materials have been reported, but the design principle of the assistant dopants for the hyperfluorescence has not been clarified, yet this is essential for developing efficient assistant dopants for hyperfluorescence.

In this work, two assistant dopants for hyperfluorescence, (4-(9,9-dimethylacridin-10(9H)-yl)phenyl)(phenyl)methanone (BPAc) and (4-(9H-carbazol-9-yl)phenyl)(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)methanone (BPAcCz), were synthesized using a benzophenone acceptor and a dimethylacridane donor to establish the design principle of the assistant dopants. The assistant dopant possessing a distorted backbone structure without any small dihedral angle donor unit is appropriate to enhance the EQE of the hyperfluorescence device by suppressing Dexter energy transfer. The green hyperfluorescence OLEDs assisted by the BPAc assistant dopant attained a high EQE of 16.6%, compared with 15.0% of the BPAcCz-assisted device.

2. Results and Discussion

Two assistant dopants, BPAc and BPAcCz, were synthesized to establish the design principle of the assistant dopant for the hyperfluorescent OLEDs. The BPAc material has only a benzophenone acceptor and a dimethylacridane donor, whereas
BPACz has an extra carbazole donor in the BPAC backbone structure. The BPAC structure is used to provide a small singlet–triplet energy splitting ($\Delta E_{ST}$) due to the strong donor character of dimethylacridane and the strong charge transfer (CT) character due to the perpendicular orientation of the donor. Although the carbazole donor is added to the BPAC structure, the carbazole may not change the emission energy of the assistant dopant because the carbazole is a weaker donor than the dimethylacridane. Instead, the carbazole donor extends the molecular structure with a small dihedral angle. Therefore, the comparison of the BPAC and BPACZ assistant dopants may reveal the design rule of the optimal assistant dopant for high EQE in the hyperfluorescent OLEDs.

The synthesis of BPAC and BPACZ is briefly shown in Scheme 1 and the detailed procedures are explained in the Experimental Section, Supporting Information. BPAC was prepared by simple Pd-catalyzed reaction between (4-bromophenyl)(phenyl)methanone and 9,9-dimethyl-9,10-dihydroacridine at a production yield of 84% after purification. The synthesis of BPACZ was initiated by the mono substitution of carbazole to the bis(4-fluorophenyl)methanone starting material using cesium carbonate, followed by reaction with bis(4-fluorophenyl)methanone. The production yield of BPACZ was 61%. The two materials were purified by sublimation to afford pure final products. Identification tools of BPAC and BPACZ were $^1$H and $^{13}$C nuclear magnetic resonance spectrometer and mass analysis.

The study goal of examining the effect of geometry in the assistant dopant was attained by studying the optimized geometry of BPAC and BPACZ by Gaussian simulation. The optimized geometrical structures of BPAC and BPACZ are shown in Figure 1. The dihedral angle between the benzophenone acceptor and dimethylacridane donor is close to 89° in the two materials, compared with 49° between carbazole and benzophenone. The carbazole donor is not greatly distorted from the benzophenone plane due to weak steric hindrance. The small dihedral angle between carbazole and benzophenone may induce facile stacking between BPACZ molecules or between BPAC and benzophenone. In contrast, BPAC has a completely twisted structure because of large steric hindrance between the hydrogens of dimethylacridane and benzophenone, which may hinder the molecular stacking between BPAC molecules or BPAC with other molecules. Our expectation that BPAC and BPACZ would have different geometries was verified by the calculated geometrical structure of the two materials.

In the optimized geometrical structure, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were determined by frontier molecular orbital calculation using B3LYP 6–31G basis set. The electronic orbital distribution in Figure 2 shows that the HOMO and LUMO distributions of BPACZ are not affected by the carbazole unit. The dimethylacridane was the HOMO determining unit and benzophenone was the LUMO dispersing unit in the two emitters. This result suggests that the carbazole unit may have little effect on the photophysical performances and energy levels of the assistant dopants.

We further expected the two assistant dopants to have similar singlet and triplet energy because different emission energies may alter the energy transfer process between the assistant
dopants and final fluorescent emitter in the hyperfluorescence process. Therefore, the emission energy of BPAc and BPACz was analyzed by measuring fluorescence and phosphorescence. The fluorescent and phosphorescent spectra of BPAc and BPACz are shown in Figure 3. The emission spectra were obtained at 77 K using tetrahydrofuran (THF) solution of the two materials. The fluorescent spectra were obtained without delay time, whereas the phosphorescent spectra were gathered after a 1 μs delay. The singlet energy/triplet energy/ΔE_ST calculated from the onset energy of the emission spectra was 3.00/2.84/0.16 and 2.97/2.83/0.14 eV in the BPAc and BPACz assistant dopants, respectively. The two materials exhibited similar singlet energy, triplet energy, and ΔE_ST, which justified our assumption of equivalence, except for the geometry of the molecular structure.

We further confirmed the photophysical similarity of the two materials by measuring the photoluminescence quantum yield (PLQY) and decay time. The absolute PLQYs of BPAc and
BPAc and BPAcCz under nitrogen were 0.72 and 0.69, respectively. The prompt fluorescence decay and delayed fluorescence decay by TADF process are compared in Figure 4. The prompt and delayed fluorescence decay data were in agreement each other, resulting in similar decay time in the two materials. The prompt/delayed fluorescence lifetime of BPAc and BPAcCz was 33.07 ns/5.23 μs and 24.65 ns/4.56 μs, respectively. As the decay time is affected by the HOMO/LUMO overlap and ΔE_ST, which were similar in the two materials. The PL decay behavior of BPAc and BPAcCz was also comparable. The reverse intersystem crossing (RISC) rate constants of BPAc and BPAcCz were 5.75/C2 105 and 5.91/C2 105 s/C0 1, respectively.[20] From the photophysical measurements, we verified that the BPAc and BPAcCz assistant dopants performed similarly as TADF emitters. All photophysical data are shown in Table 1.

In addition to the photophysical equivalency, the electrochemical similarity was examined by analyzing the oxidation and reduction potentials of BPAc and BPAcCz. The electrochemical oxidation and reduction scan data collected by voltage scan from cyclic voltammetry are shown in Figure 5. The oxidation and reduction onsets were observed at similar voltages, which demonstrated the electrochemical consistency of the two materials. The HOMO/LUMO of BPAc and BPAcCz estimated from the electrochemical measurements to be −5.71/−3.30 eV, respectively.

Based on the photophysical and electrochemical matching of BPAc and BPAcCz, BPAc- and BPAcCz-based TADF devices were prepared for comparison. They were doped in the bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) host at a doping concentration of 10–30%. The EQE-luminance data of the BPAc and BPAcCz TADF devices are shown in Figure 6. Other basic device data, including current density–voltage and luminance–voltage characteristics, are shown in Figure S1, Supporting Information. The EQE at 100/1000 cd m−2 was 18.1/16.5% and 19.5/15.9% in the BPAc and BPAcCz devices at 10% doping concentration, respectively. The two materials performed similarly, even in the TADF OLEDs by the similar photophysical properties.

![Figure 4. The transient PL decay curves of a) prompt and b) delayed components of BPAc and BPAcCz.](image)

![Figure 5. The measured electrochemical oxidation and reduction curves of BPAc and BPAcCz.](image)

**Table 1. The photophysical properties of BPAc and BPAcCz.**

|       | λ_{abs} [eV] | E_S [eV] | Φ_T [ %] | Φ_p [ %] | τ_p [ns] | τ_d [μs] | k_p [10^7 s/C0 1] | k_d [10^4 s/C0 1] | k_{ISC} [10^7 s/C0 1] | k_{RISC} [10^5 s/C0 1] |
|-------|--------------|----------|-----------|-----------|-----------|-----------|-----------------|-----------------|-----------------|-----------------|
| BPAc  | 2.86         | 3.00     | 2.84      | 72        | 21        | 52        | 33.1            | 5.2             | 3.02            | 1.9             |
| BPAcCz| 3.21         | 2.97     | 2.83      | 69        | 47        | 47        | 24.7            | 4.1             | 4.06            | 2.2             |

a) Measured in distilled THF at 1.0 × 10−3 M solution; b) Determined from the onset of spectra and measured in distilled THF solution at 77 K; c)Measured under N2 atmosphere using 5 wt% TADF emitter-doped DPEPO films on quartz substrate; d)Obtained by integrating prompt component.
doping concentration of the 6tBPA ranged from 0% to 1%. The basic device data are shown in Figure S2, Supporting Information, and the EQE–current density results are shown in Figure 7. The EQE change of the BPAc and BPAcCz devices according to 6tBPA doping concentration was different in the hyperfluorescent OLEDs. The EQE of the hyperfluorescent OLEDs for the BPAc devices was slightly decreased from 16.2% to 15.8% by increasing the 6tBPA doping concentration from 0% to 1%, compared with a decrease from 16.5% to 14.4% at the same condition for the BPAcCz-based hyperfluorescent OLEDs. Although the EQE of the pristine TADF devices of BPAc and BPAcCz was similar, that of the hyperfluorescent OLEDs was not.

We partially attributed this EQE difference to the PLQY of the 6tBPA-doped BPAc and BPAcCz emitting layers: 96.8% and 88.4%, respectively. The high PLQY is partially responsible for the high EQE of the 6tBPA-doped BPAc device. Another reason is the energy transfer process between the assistant dopants and the fluorescent emitter. The major energy transfer process of the hyperfluorescent OLEDs is Förster energy transfer from the assistant dopant to the fluorescent emitter. The Förster energy transfer process of the hyperfluorescent OLEDs is Förster energy transfer from the assistant dopant to the fluorescent emitter. However, the Dexter energy transfer from the assistant dopant to the fluorescent emitter can be different. As the doping concentration of the assistant dopant and the fluorescent emitter was the same in the BPAc- and BPAcCz-based hyperfluorescent OLEDs, it is the Dexter energy transfer that differentiates the loss process between the two devices.

The transient PL decay of the blue fluorescent emitter-doped film was measured to study Dexter energy transfer. The blue fluorescent dopant was 9-((1,1’,2’,1”-terphenyl)-2-yl)-10-phenylandathracene (AnTP).[21] The Dexter energy transfer process from the BPAc and BPAcCz assistant dopants to the AnTP emitter was analyzed by transient PL measurement. Two samples to identify the Dexter energy transfer were DPEPO:BPAc:AnTP and DPEPO:BPAcCz:AnTP films. The AnTP-doped system allowed only Dexter energy transfer, but Förster energy transfer is prohibited between the assistant dopants and emitter due to the large singlet energy of the blue fluorescent emitter. The transient PL decay of the AnTP-doped system of BPAc and BPAcCz dispersed in the DPEPO host at a doping concentration of 20 and 1 wt% is shown in Figure 8. In contrast to the similar decay profiles of the DPEPO:BPAc and DPEPO:BPAc:AnTP films, the decay of DPEPO:BPAcCz:AnTP was accelerated compared with that of DPEPO:BPAcCz, as reflected in the decay time reduction from 3.05 to 2.11 μs with addition of AnTP. The sharp decrement of the decay time of BPAcCz after AnTP indicates triplet exciton quenching by the AnTP emitter. The triplet exciton quenching by
Dexter energy process was less significant in BPAc than in BPAcCz.

The EL spectra of the BPAc and BPAcCz hyperfluorescent OLEDs are shown in Figure 9. The energy transfer from the assistant dopants to 6tBPA was enhanced at 1% doping concentration and 6tBPA emission was dominantly observed. However, the TADF emission of the sensitizers continued due to incomplete energy transfer. The color coordinates of the BPAc- and BPAcCz-based OLEDs were (0.24, 0.54) and (0.25, 0.55), respectively. All device results are shown in Table 2.

3. Conclusions

We have presented a superior design principle using an assistant dopant to increase the EQE of the hyperfluorescent OLEDs by comparing two assistant dopants with different geometrical structures. The assistant dopant with only a distorted backbone structure maintained the original EQE of the assistant dopant by minimizing the loss process, but the assistant dopant with an additional nondistorted structure reduced the EQE of the hyperfluorescent OLEDs by activating the loss process of Dexter energy transfer.
transfer. Therefore, the assistant dopants for the hyperfluorescent OLEDs need to have a distorted backbone structure to suppress the loss mechanism in the energy transfer process.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
assistant dopants, efficiencies, hyperfluorescence, organic light-emitting diodes, thermally activated delayed fluorescence

Received: October 24, 2020
Revised: February 1, 2021
Published online: March 10, 2021

[1] C. W. Tang, S. A. VanSlyke, Appl. Phys. Lett. 1987, 51, 913.
[2] K. Okumoto, H. Kanno, Y. Hamaa, H. Takahashi, K. Shibata, Appl. Phys. Lett. 2006, 89, 063504.
[3] Y. S. Yao, Q. X. Zhou, X. S. Wang, Y. Wang, B. W. Zhang, Adv. Funct. Mater. 2007, 17, 93.
[4] G. Li, J. Shinar, Appl. Phys. Lett. 2003, 83, 5359.
[5] M. Zhu, C. Yang, Chem. Soc. Rev. 2013, 42, 4963.
[6] M. A. Baldo, D. F. O’Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, Nature 1998, 395, 151.
[7] C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, J. Appl. Phys. 2001, 90, 5048.
[8] A. Endo, K. Sato, K. Yoshimura, T. Kai, A. Kawada, H. Miyazaki, C. Adachi, Appl. Phys. Lett. 2011, 98, 083302.
[9] K. Goushi, K. Yoshida, K. Sato, C. Adachi, Nat. Photonics 2012, 6, 253.
[10] K. Goushi, C. Adachi, Appl. Phys. Lett. 2012, 101, 023306.
[11] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Nature 2012, 492, 234.
[12] H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda, C. Adachi, Nat. Commun. 2014, 5, 4016.
[13] A. Kretzschmar, C. Patze, S. T. Schwaebel, U. H. F. Bunz, J. Org. Chem. 2015, 80, 9126.
[14] D. R. Lee, S. H. Hwang, S. K. Jeon, C. W. Lee, J. Y. Lee, Chem. Commun. 2015, 51, 8105.
[15] D. Zhang, M. Cai, Y. Zhang, D. Zhang, L. Duan, Mater. Horiz. 2016, 3, 145.
[16] D. Zhang, L. Duan, C. Li, Y. Li, H. Li, D. Zhang, Y. Qiu, Adv. Mater. 2014, 26, 5050.
[17] D. Zhang, X. Song, M. Cai, L. Duan, Adv. Mater. 2018, 30, 1705250.
[18] M. A. Baldo, M. E. Thompson, S. R. Forrest, Nature 2000, 403, 750.
[19] D. D. Zhang, L. Duan, Y. Li, H. Y. Li, Z. Y. Bin, D. Q. Zhang, J. Qiao, G. D. Dong, L. D. Wang, Y. Qiu, Adv. Funct. Mater. 2014, 24, 3551.
[20] K. Masui, H. Nakanotani, C. Adachi, Org. Electron. 2013, 14, 2721.
[21] J. S. Jang, S. H. Han, H. W. Choi, K. S. Yook, J. Y. Lee, Org. Electron. 2018, 59, 236.