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Management of thermally activated delayed fluorescence using a secondary electron accepting unit in thermally activated delayed fluorescent emitters

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Abstract

A molecular design approach adopting secondary electron accepting units in addition to a main electron acceptor was investigated as a strategy to manage the thermally activated delayed fluorescent (TADF) performances of the emitters. A main skeleton possessing a benzofurocarbazole donor, a phenyl linker and a t-butylated diphenyltriazine acceptor was a platform of the molecular structures for high efficiency in the TADF devices and CN units was attached to the phenyl linker as the secondary accepting unit. Either one or two CN units were introduced to examine the effect of the number of secondary electron accepting unit with the emission properties of the TADF emitters revealed that the introduction of one CN secondary electron accepting unit is ideal in terms of TADF performances of the emitters. The TADF emitter without the CN secondary acceptor realized one of the highest efficiency of 19.0% in the deep blue TADF devices with a y color coordinate below 0.10 by introducing the t-butylated

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diphenyltriazine acceptor. Whereas, the TADF emitter with one CN secondary electron accepting unit displayed even higher external quantum efficiency of 26.6%.

Key words : electron acceptor, delayed fluorescence, efficiency, emission color

Introduction

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The progress of thermally activated delayed fluorescent (TADF) organic light-emitting diodes (OLEDs) has been remarkable for the last several years with the advent of molecular structures allowing the up-conversion of triplet excitons into singlet excitons.¹⁻⁹ The core structure for the up-conversion process is the donor-acceptor (D-A) backbone structure because it can minimize the energy difference between singlet and triplet excited states by stabilizing the singlet excited state using a charge transfer (CT) emission process rather than the local emission (LE) process which is common in conventional fluorescent emitters.^{2, 5, 7, 10-12} Therefore, the main backbone structure of the TADF dopants was mostly derived from the D-A structure.

Although the main D-A skeleton was shared in the TADF molecular design, the chemical structure of the TADF emitters was diversified by engineering the arrangement of the donor and acceptor units to manage the TADF characteristics. For example, D-A-D type backbone structure with an additional donor unit and A-D-A structure with an extra acceptor unit could increase the external quantum efficiency (EQE) of the TADF devices.^{2, 4, 5, 7, 10, 13} Multi-donor and multi-acceptor combined structure was a modified version of the D-A structure.¹⁴⁻¹⁶ Other than these, multi-donor and one acceptor merging was also an effective approach to control the emission color and enhance EQE of the D-A base structure of the TADF emitters. Generally, the increase of the number of donors had an EQE boosting effect by large overlap of the molecular orbital for high radiative transition probability.^{7, 17, 18} In many cases, the donor part rather than the acceptor part of the TADF emitters was managed. However, the acceptor part of the TADF emitter is as important as the donor part because the emission from the TADF emitter is CT emission from the donor to acceptor and the key parameter of singlet-triplet energy gap (ΔE_{ST}) is governed by both the donor and acceptor.^{1-10, 12} Therefore, it is essential to engineer the acceptor part of the TADF emitter for enhanced TADF performances.

Herein, we describe the molecular design approach introducing secondary acceptor units in addition to a main acceptor as a strategy to manage the TADF properties of the TADF emitters. The main acceptor

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of the TADF emitter was t-butylated diphenyltriazine and the secondary acceptor was a CN unit. View Article Online DOI: 10.1039/C9TC01354G Correlation of the number of secondary electron accepting unit with the emission properties of the TADF emitters revealed that the introduction of one CN secondary electron accepting unit is ideal in terms of TADF performances of the emitters. The pristine molecule without the CN unit showed high EQE of 19.0% with a color coordinate of (0.15, 0.09) and achieved one of the highest EQEs of the deep blue TADF devices with a y color coordinate below 0.10. The TADF emitter with one CN secondary electron accepting unit displayed even higher EQE of 26.6%.

Results and discussion

The design concept of the TADF emitter introducing the secondary acceptor in the D-A backbone structure is to precisely manage the TADF properties by additionally attaching weaker acceptors than the main acceptor. As the main acceptor is a strong acceptor, the intrinsic acceptor character of the main acceptor can be maintained and the secondary acceptor can adjust the electron acceptor character for improved performances. Main skeleton of the TADF emitters was the D-A structure with a phenyl linker between the donor and acceptor units, where the donor was benzofurocarbazole and the acceptor was t-butylated diphenyltriazine. The secondary acceptor was the CN unit which is weaker than diphenyltriazine as the electron acceptor. The secondary acceptor was attached to the phenyl linker connecting the donor and acceptor. The number of the CN secondary acceptor was controlled from 0 to 2 to examine the effect of the secondary acceptor on the TADF properties.

The chemical structures and synthetic processes of the TADF emitters with the CN secondary acceptors, TrzBFCz, TrzCNBFCz, and Trz2CNBFCz are shown in **Scheme 1**. The TrzBFCz has the conventional D-A structure, the TrzCNBFCz has one CN secondary acceptor in the D-A structure, and the Trz2CNBFCz has two CN secondary acceptors in the D-A structure. As the number of the CN secondary acceptors was systematically controlled, the effect of the secondary acceptor on the TADF performances can be examined using the three TADF emitters. The synthesis of the TrzBFCz was simply

carried out by NaH mediated amination reaction between benzofurocarbazole and 2.4-bis(4-(tert-View Article Online butyl)phenyl)-6-(4-fluorophenyl)-1,3,5-triazine prepared by Suzuki coupling reaction between 2,4-bis(4-(tert-butyl)phenyl)-6-chloro-1,3,5-triazine and (4-fluorophenyl)boronic acid. The synthetic process of the TrzCNBFCz was quite similar to that of the TrzBFCz except that (3-cyano-4-fluorophenyl)boronic acid was adopted instead of (4-fluorophenyl)boronic acid in the preparation of the 5-(4,6-bis(4-(tertbutyl)phenyl)-1,3,5-triazin-2-yl)-2-fluorobenzonitrile intermediate. However, the Trz2CNBFCz could not be obtained from the same synthetic process because 5-(4,6-bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2yl)isophthalonitrile intermediate for amination reaction was not available by direct Suzuki coupling reaction. In this case, a two-step synthetic method employing a Suzuki coupling reaction between 2,4bis(4-(tert-butyl)phenyl)-6-chloro-1.3.5-triazine 5-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2and yl)isophthalonitrile followed by lithiation using Lithium diisopropylamide to generate a Br functional unit between two CN units was used. Final reaction step was CuI mediated amination reaction between 5-(4,6-bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)-2-bromoisophthalonitrile and benzofurocarbazole. Work-up and purification processes including extraction, column chromatography, recrystallization and vacuum sublimation provided the pure final products. Conventional chemical analysis methods of 1 H and ¹³C nuclear magnetic resonance (NMR), mass analysis, and high performance liquid chromatography identified the TADF emitters.

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Scheme 1. Synthesis scheme of TrzBFCz, TrzCNBFCz and Trz2CNBFCz

Electronic molecular orbital distribution of the TADF emitters was examined to study the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) change by the CN secondary acceptors. The calculation results by Gaussian software using the B3LYP 6-31G basis set pictured the HOMO and LUMO of the TADF emitters in **Figure 1**. Overall pictures of the HOMO and LUMO look quite similar in the three TADF emitters in that the HOMO and LUMO are extensively separated, but minor change of the HOMO and LUMO was noticed by the CN secondary acceptor. The addition of the CN secondary acceptor localized the HOMO of the TADF materials. The HOMO of the TrzBFCz and TrzCNBFCz was largely extended from the benzofurocarbazole donor to the phenyl linker, but the HOMO extension became narrow in the Trz2CNBFCz. The LUMO dispersion was also further localized as the number of CN unit is increased. In the case of the TrzBFCz, the LUMO was distributed

from the diphenyltriazine unit to the phenyl linker, but it was spread over the triazine unit and phenyl View Article Online DOI: 10.1039/C9TC01354G linker without any dispersion on the phenyl unit of the diphenyltriazine in the Trz2CNBFCz. The HOMO and LUMO change can be interpreted as the effect of the electron withdrawing character of the CN unit. The HOMO was not widely extended from the donor to the phenyl linker by the electron deficiency of the CN attached phenyl linker, whereas the LUMO was shifted to the phenyl linker by the electron deficiency. The oscillator strength of the TrzBFCz, TrzCNBFCz and Trz2CNBFCz was 0.3341, 0.2195 and 0.1250, respectively. The addition of second CN unit reduced the oscillator strength due to the isolation of the HOMO and LUMO.



Figure 1. Ground state orbital distribution of TrzBFCz, TrzCNBFCz and Trz2CNBFCz calculated with B3LYP 6-31G basis set

The orbital distribution of the three materials was also estimated in singlet and triplet excited states. **Figure 2** pictured the highest occupied natural transition orbital (HONTO) and the lowest unoccupied natural molecular orbital (LUNTO) of TrzBFCz, TrzCNBFCz and Trz2CNBFCz emitters. In all three emitters, the HONTO and LUNTO in singlet excited state were spatially separated, reflecting the charge transfer (CT) nature of the singlet emission. However, the HONTO and LUNTO in triplet excited state were dissimilar in the three emitters. The large overlap of the HONTO and LUNTO was featured in the TrzBFCz, but the overlap was significantly reduced by the CN secondary acceptor in the TrzCNBFCz view Article Online and Trz2CNBFCz, suggesting that the origin of the lowest triplet excited state is CT state.

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Figure 2. Excited state orbital distribution of TrzBFCz, TrzCNBFCz and Trz2CNBFCz calculated with B3LYP 6-31G basis set

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Figure 3. Optimized Structure of TrzBFCz, TrzCNBFCz and Trz2CNBFCz in ground state and excited state.

In addition to the orbital distribution, the geometrical structure of the TADF emitters was affected by the CN secondary acceptor. The optimized geometrical structure of the three emitters in ground state and excited state are shown in **Figure 3**. The dihedral angles between the benzofurocarbazole donor and the phenyl unit were 53.0, 56.5 and 66.9 ° in the TrzBFCz, TrzCNBFCz and Trz2CNBFCz emitters in ground state. The CN unit distorted the benzofurocarbazole donor from the phenyl plane by weak steric hindrance. The benzofurocarbazole donor of TrzCNBFCz and Trz2CNBFCz was largely distorted in excited state, affording close to 90 ° dihedral angle. The perpendicular orientation of the donor from the phenyl plane agrees with the strong CT nature of the excited state. However, the dihedral angle of the TrzBFCz was only 48.3 ° in excited state, suggesting weak CT character in excited state.

The effect of the secondary acceptor can be clearly observed in the oxidation and reduction potential measurement by cyclic voltammetry (CV) to estimate the HOMO and LUMO. Both the oxidation and reduction in **Figure 4** were affected by the strongly electron withdrawing CN unit. The HOMO/LUMO levels of the TrzBFCz, TrzCNBFCz and Trz2CNBFCz were -6.04/-3.21, -6.16/-3.41, and -6.37/-4.08 eV, respectively. The HOMO and LUMO were gradually deepened by adding extra CN units. In particular,

the LUMO was largely deepened by the CN secondary acceptor, which resulted in the small HOMO-View Article Online LUMO gap in the TADF emitters with the CN secondary acceptor.



Figure 4. CV measurement of TrzBFCz, TrzCNBFCz, Trz2CNBFCz

The photophysical analysis of the TADF emitters was carried out by ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) measurements. **Figure 5(a)** shows the UV-vis absorption spectra of the three emitters in tetrahydrofuran solution. Main absorption peaks of the UV-vis spectra assigned to electronic transition of the backbone structure were analogous, but the CT absorption peaks were shifted to long wavelength according to the number of the CN secondary acceptor. The red shift of the CT absorption peaks suggests strengthened CT character of the TADF emitters by adding the CN secondary acceptor. PL emission spectra of the TADF emitters at room temperature and at low temperature (77 k) were also shifted to long wavelength in the order of TrzBFCz < TrzCNBFCz < Trz2CNBFCz. The addition of the CN unit intensified the CT character of the emitters by the augmented acceptor strength, shifting the emission spectra to long wavelength. The PL spectra at room temperature were also broadened by adding the CN secondary acceptor due to strong CT character. The origin of the

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singlet emission was CT emission from the featureless broad emission, but that of the triplet emission View Article Online DOI: 10.1039/C9TC01354G was a hybrid emission from CT and local triplet excited states. The singlet energy/triplet energy values of the TrzBFCz, TrzCNBFCz and Trz2CNBFCz emitters were 3.22/2.95, 3.04/2.91, and 2.87/2.77 eV, respectively, which afforded ΔE_{ST} values of 0.27, 0.13, and 0.10 eV. The extra CN secondary acceptor reduced the ΔE_{ST} by the strong acceptor character.





emission spectra at low temperature with 2 microsecond delay





The photophysical behaviour of the emitters was further studied by analysing the transient PL decay and absolute PL quantum yield measurements to extract kinetic parameters for the TADF transition processes. The transient PL decay data of the emitters are presented in **Figure 6(a)** and (b). The decay times for the fast fluorescence process were 8.3, 13.8, and 18.5 ns in the TrzBFCz, TrzCNBFCz and Trz2CNBFCz emitters, and those for the delayed fluorescence process were 26.3, 9.4, and 3.1 µs. The CN secondary acceptor accelerated the delayed fluorescence process, but retarded the fast fluorescence transition. The acceleration of the delayed fluorescence transition by the CN secondary acceptor is due to small ΔE_{ST} . However, the PL quantum yield of the Trz2CNBFCz was only 62.0% because of small oscillator strength caused by extensive separation of the HOMO and LUMO. As the radiative transition is activated by large HOMO and LUMO overlap, the HOMO and LUMO separation by the two strong electron withdrawing CN units limited the radiative transition probability and PL quantum yield. The PL quantum yield was close to 100% in the TrzBFCz and TrzCNBFCz due to high oscillator strength. Although it was slightly reduced in the TrzCNBFz, the reduced oscillator strength was compensated by small ΔE_{sT} . Therefore, the addition of one CN secondary acceptor was ideal to reach high PL quantum yield and shortened delayed fluorescence lifetime. As a result, the reverse intersystem crossing (RISC) rate constant of the TrzCNBFCz was much higher than that of the TrzBFCz. The rather high RISC rate

constant of the Trz2CNBFCz is due to short delayed fluorescence lifetime in spite of low PL quantum View Article Online DOI: 10.1039/C9TC01354G

| | E _{gap} (eV) | E _{HOMO} (eV) | E _{LUMO} (eV) | UV gap (eV) | E _s (eV) | E _T (eV) | ∆E _{st} (eV) | Φ_{total} | Φ_{p} | Φ_{d} | τ _p (ns) | τ _d (μs) |
|------------|--------------------------|---------------------------|---------------------------|----------------|------------------------|------------------------|--------------------------|----------------|------------|------------|------------------------|------------------------|
| TrzBFCz | 2.83 | -6.04 | -3.21 | 3.08 | 3.22 | 2.95 | 0.27 | 99.8% | 82.3% | 17.5% | 8.3 | 26.3 |
| TrzCNBFCz | 2.75 | -6.16 | -3.41 | 2.95 | 3.04 | 2.91 | 0.13 | 100.0% | 47.5% | 52.5% | 13.8 | 9.4 |
| Trz2CNBFCz | 2.29 | -6.37 | -4.08 | 2.74 | 2.87 | 2.77 | 0.10 | 62.0% | 28.1% | 33.9% | 18.5 | 3.1 |

Table 1. Summarized photophysical data of TrzBFCz, TrzCNBFCz and Trz2CNBFCz

* Uv-vis absorption spectra was measured in THF solution with 10⁻⁵M concentration

** Singlet and triplet energy was calculated from onset of low temperature emission spectra in frozen THF matrix at 77K without and with 2 ms delay time.

*** PLQY and transient PL was measured with the DPEPO film doped 10 wt% of emitters in N2 atmosphere.

**** Prompt component and delayed component was calculated by integrating transient PL data.



Figure 7. (a) Current density-Voltage-Luminance curves, (b) Quantum Efficiency-Luminance curves and (c) Electroluminescence spectra of TrzBFCz device

The TADF devices of the three emitters were fabricated by doping in the common (oxybis(2,1-phenylene))bis(diphenylphosphine oxide) (DPEPO) host. The doping concentration range of the TADF emitters was from 10% to 30%. Firstly, the device performances of the pristine TrzBFCz without the CN units were investigated. All device performances including current density (J)-voltage (V), luminance (L)-V, EQE-L, and electroluminescence (EL) spectra of the TrzBFCz devices are in **Figure 7** according

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to doping concentration. A general trend showing the increase of J and L according to doping View Article Online DOI: 10.1039/C9TC0 concentration was noticed by carrier hopping through the dopant molecules as reported in other DPEPO hosted TADF devices.²⁰ The carrier trapping effect can be confirmed in the energy level diagram in Figure 8. The EQE was optimized as 19.0% at 10% doping concentration and then reduced according to the doping concentration by concentration quenching effect. Considering that the color coordinate of the TrzBFCz device was (0.15, 0.09), the 19.0% EQE of the TrzBFCz device is one of the highest EQEs of the deep blue TADF OLEDs with a v color coordinate below 0.10. Compared with the TADF emitter which had a diphenyltriazine acceptor without the t-butyl unit, the y color coordinate was shifted from 0.18 to 0.09 by the electron donating character of the t-butyl group.¹⁹ The EQE was also increased from 16.4% to 19.0% possibly due to intermolecular interaction suppressing role of the t-butyl unit in the diphenyltriazine acceptor. In the EL spectra, peak wavelength of the device was 447 nm at 10% doping concentration and it was shifted to 453 nm at 30% doping concentration. The bathochromic shift of the EL spectra at high doping concentration was marginal because of the weak CT character and t-butyl blocking groups in the acceptor unit. The color coordinates of the TrzBFCz devices were (0.15, 0.09), (0.15, 0.10), and (0.15, 0.11) at 10, 20, and 30% doping concentrations.



Figure 8. Energy level diagram of TrzBFCz, TrzCNBFCz and Trz2CNBFCz devices

The device data of the TrzCNBFCz and Trz2CNBFCz devices are shown in **Figure 9** and **10**. The J

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Figure 9. (a) Current density-Voltage-Luminance curves, (b) Quantum Efficiency-Luminance curves and (c) Electroluminescence spectra of TrzCNBFCz device

The EL spectra shift according to doping concentration was observed in the TADF devices by polar interaction between dopant molecules. The strong donor-acceptor type TrzCNBFCz and Trz2CNBFCz showed large red shift of the emission spectra at high doping concentration compared with the weak donor-acceptor type TrzBFCz. A large red shift of the EL spectra by adding the CN secondary acceptor was noticed by the strengthened CT character. At 10 wt% doping concentration, the peak wavelengths

of the TrzCNBFCz and Trz2CNBFCz devices were 473 and 511 nm, respectively, which corresponded View Article Online DOI: 10.1039/C9TC01354G to color coordinates of (0.16, 0.24) and (0.27, 0.52). All device performances were summarized in **Table**

2. Current efficiency and power efficiency of the devices are in supporting information.



Figure 10. (a) Current density-Voltage-Luminance curves, (b) Quantum Efficiency-Luminance curves and (c) Electroluminescence spectra of Trz2CNBFCz device

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|------------------|---------------------------|---------------|--------------|--------------------------|-----------------|--|
| | $\mathbf{V}_{\mathbf{d}}$ | EL spectrum | CIE | QE (%) | | |
| | (V) | (nm) | CIE | [1000cd/m ²] | [Max] | |
| TrzBFCz (10%) | 8.1 | 447 | (0.15, 0.09) | 4.3 | 19.0 | |
| TrzBFCz (20%) | 6.9 | 451 | (0.15, 0.10) | 8.0 | 18.0 | |
| TrzBFCz (30%) | 5.3 | 453 | (0.15, 0.11) | 8.3 | 13.1 | |
| FrzCNBFCz (10%) | 10.2 | 473 | (0.16, 0.24) | 5.9 | 20.9 | |
| rzCNBFCz (20%) | 6.5 | 481 | (0.17, 0.31) | 16.8 | 26.6 | |
| FrzCNBFCz (30%) | 6.0 | 482 | (0.17, 0.33) | 14.8 | 21.8 | |
| Frz2CNBFCz (10%) | 9.0 | 511 | (0.27, 0.52) | 6.9 | 15.8 | |
| rz2CNBFCz (20%) | 7.0 | 524 | (0.33, 0.57) | 10.1 | 13.7 | |
| rz2CNBFCz (30%) | 6.9 | 528 | (0.35, 0.58) | 7.4 | 9.2 | |

Table 2. Summarized device data of TrzBFCz, TrzCNBFCz and Trz2CNBFCz devices

* V_d: Driving voltage at 1,000 cd/m²

** All data was measured at 1000 cd/m²

Conclusions

Three TADF emitters based on the molecular platform of t-butylated diphenyltriazine acceptor, a phenyl linker, and benzofurocarbazole donor combined with a CN secondary electron accepting unit were synthesized to study the effect of the CN secondary acceptor on the TADF properties. Main role of the CN secondary accepting unit was to increase the RISC rate constant for efficient up-conversion. The addition of one CN secondary acceptor facilitated the RISC process while maintaining the high PL quantum yield of the pristine TADF emitter, enabling high EQE of 26.6% in the sky-blue TADF devices. However, the addition of two secondary acceptors reduced the PL quantum yield of the TADF emitter, resulting in low EQE. Moreover, the pristine molecular design having the t-butylated diphenyltriazine acceptor achieved high EQE of 19.0% with a color coordinate of (0.15, 0.09), which is one of the highest EQEs of the deep blue TADF OLEDs with a y color coordinate below 0.10. Therefore, the molecular design approach introducing the secondary acceptor is useful to manage the RISC process while keeping high PL quantum yield of the emitters.

Experimental

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General information

2,4-bis(4-(tert-butyl)phenyl)-6-chloro-1,3,5-triazine, 5H-benzofuro[3,2-c]carbazole were synthesized in our previous work. (3-cyano-4-fluorophenyl)boronic acid, 5-bromoisophthalonitrile was supplied from LG Chem. Ltd. Bis(pinacolate) diboron was purchased from INCO Co. (4-fluorophenyl)boronic acid, 1,2-dibromotetrachloroethane were products of Alfa Aesar, Thermo Fisher Scientific Inc. [1,1'bis(diphenylphosphino)ferrocene]palladium(II) dichloride, tetrakis(triphenylphosphine) palladium(0) were purchased from P&H Tech Co. Sodium hydride, Copper iodide, lithium diisopropylamide, (±)trans-1,2-diaminocyclohexane were products of Sigma Aldrich Co. Potassium acetate, potassium carbonate, cesium carbonate, 1,4-dioxane, N,N-dimethylformamide (DMF) were supplied from Duksan Sci. Co. n-hexane, methylene chloride, tetrahydrofuran, chloroform were purchased from Samchun Pure Chemical Co., Ltd. Tetrahydrofuran (THF) was distilled over sodium and calcium hydride. UV-vis spectrophotometer (JASCO, V-730) was used to measure absorption spectra of each emitters. The mass spectrometry was measured using Advion, Expression^L CMS spectrometer with APCI mode. The HOMO and LUMO were measured and calculated by using a cyclic voltammetry (Ivium Tech., Iviumstat). The PL spectra was measured with a fluorescence spectrophotometer (PerkinElmer, LS-55). The singlet and triplet energy of each emitters was determined from frozen THF solution at 77K with and without 2 ms delay time. ¹H-nuclear magnetic resonance (NMR) and ¹³C-NMR were analyzed by using AVNACE III HD (Bruker, 500 MHz) spectrometer. The PL quantum yield and transient PL data were obtained by using Quantaurus-QY system (Hamamatsu, C11347-11) and Quantaurus-Tau system (Hamamatsu, C11367-31) under N₂ atmosphere.

Synthesis

2,4-Bbis(4-(tert-butyl)phenyl)-6-(4-fluorophenyl)-1,3,5-triazine

2,4-Bis(4-(tert-butyl)phenyl)-6-chloro-1,3,5-triazine (1.50 g, 3.95 mmol) and (4-fluorophenyl)boronic acid (0.83 g, 5.92 mmol) were dissolved in tetrahydrofuran solvent (20 ml) and directly poured into 2-neck round-bottom flask. Then potassium carbonate was dissolved in deionized water (10 ml) at 2M

concentration and injected into mixed solution of the starting materials. After slight heating for 10 min,

tetrakis(triphenylphosphine) palladium(0) (0.14 g, 0.12 mmol) was poured into the reaction mixture and refluxed for 12 h. After cooling down to room temperature, the reaction mixture was extracted using methylene chloride. Extracted organic layer was then concentrated and adsorbed into silica gel. Adsorbed mixture was purified with column chromatography using eluent solvent (methylene chloride: n-hexane=1:4). A white powder was obtained after all purification processes. (1.31 g, Yield 75%)

¹H NMR (500 MHz, CDCl₃) : δ 8.79-8.76 (m, 2H), 8.66 (d, 4H, J=9.0 Hz), 7.59 (d, 4H, J=7.0 Hz), 7.25-7.21 (m, 2H), 1.40 (s, 18H), MS (APCI) m/z: Found 440.2 [(M+H)⁺] ; Calculated for C₂₉H₃₀FN₃, 439.57

5-(4-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)phenyl)-5H-benzofuro[3,2-c]carbazole (TrzBFCz)

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Sodium hydride (0.16 g, 6.82 mmol) was added into a pressure tube. Then DMF (3 ml) was added into the pressure tube. 5H-benzofuro[3,2-c]carbazole (0.70 g, 2.73 mmol) was dissolved in DMF (5 ml) and poured into the pressure tube. After 30 min with stirring, 2,4-bis(4-(tert-butyl)phenyl)-6-(4-fluorophenyl)-1,3,5-triazine (1.00g, 2.27 mmol) in DMF (10 ml) was injected into the reaction solution and the mixture was refluxed for 24 h. After the reaction, deionized water was poured into the reaction mixture for sodium hydride quenching. Then the mixture was extracted using chloroform. Separated organic layer was concentrated by rotary evaporator and the crude product was purified with column chromatography using eluent solvent (Chloroform: n-hexane=1:1). Final product was purified using train sublimation. A greenish powder was obtained after all purification. (0.81 g, Yield 53%)

¹H NMR (500 MHz, CDCl₃) : δ 9.00 (d, 2H, J=7.0 Hz), 8.71 (d, 4H, J=7.0 Hz), 8.58 (d, 1H, J=7.5 Hz), 7.96 (d, 1H, J=7.0 Hz), 7.93 (d, 1H, J=8.5 Hz), 7.82 (d, 2H, J=6.75 Hz), 7.73 (d, 1H, J=8.0 Hz), 7.62-7.57 (m, 5H), 7.50 (t, 2H, J=8.0 Hz), 7.44 (t, 1H, J=7.75 Hz), 7.37 (t, 1H, J=7.0 Hz), 1.41 (s, 18H), ¹³C NMR (125 MHz, CDCl₃) : δ 171.9, 170.8, 156.5, 156.4, 151.4, 141.5, 141.1, 140.4, 135.8, 133.7, 130.8, 129.1, 127.2, 126.2, 125.9, 125.6, 125.2, 123.1, 123.0, 121.6, 121.2, 120.0, 118.3, 117.1, 111.9, 110.2, 109.3, 105.8, 35.3, 31.5, MS (HR-FAB+) m/z: Found 677.3277 [(M+H)⁺]; Calculated for C₄₇H₄₀N₄O,

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5-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)-2-fluorobenzonitrile

Synthetic method of 5-(4,6-bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)-2-fluorobenzonitrile was almost same that of 2,4-bis(4-(tert-butyl)phenyl)-6-(4-fluorophenyl)-1,3,5-triazine except that (3-cyano-4fluorophenyl)boronic acid (0.98 g, 5.92 mmol) was used as the starting material instead of (4fluorophenyl)boronic acid. A white powder was obtained after purification (1.70 g, Yield 93%). ¹H NMR (500 MHz, CDCl₃) : δ 9.04 (d, 1H, J=6.5 Hz), 9.00-8.97 (m, 1H), 8.64 (d, 4H, J=6.75 Hz), 7.61 (d, 4H, J=7.5 Hz), 7.39 (t, 1H, J=8.5 Hz), 1.41 (s, 18H), MS (APCI) m/z: Found 465.2 [(M+H)⁺]; Calculated for C₃₀H₂₉FN₄, 464.58

2-(5H-benzofuro[3,2-c]carbazol-5-yl)-5-(4,6-bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-

yl)benzonitrile (TrzCNBFCz)

5-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (1.00 g, 2.15 mmol), 5Hbenzofuro[3,2-c]carbazole (0.66 g, 2.58 mmol) and cesium carbonate (2.10 g, 6.46 mmol) were added into a pressure tube. Then DMF (15 ml) was added into the mixture. After that, the reaction was proceeded at reflux condition for 12 h. The reaction mixture was cooled down to room temperature and extracted using chloroform. The extracted organic layer was evaporated using a rotary evaporator and adsorbed into a silica gel. The adsorbed crude product was purified by using column chromatography. After column purification, the final product was sublimated using vacuum sublimation. After all purification, a bright green powder was obtained. (1.21 g, Yield 80%)

¹H NMR (500 MHz, CDCl₃) : : δ 9.33 (s, 1H), 9.16 (d, 1H, J=8.0 Hz), 8.70 (d, 4H, J=7.0 Hz), 8.59 (d, 1H, J=7.5 Hz), 7.98-7.96 (m, 2H), 7.86 (d, 1H, J=8.5 Hz), 7.74 (d, 1H, J=8.5 Hz), 7.63 (d, 4H, J=7.0 Hz), 7.54-7.44 (m, 3H), 7.38 (t, 2H, J=7.0 Hz), 7.28 (d, 1H, J=8.5 Hz), 1.42 (s, 18H), ¹³C NMR (125 MHz, CDCl₃) : δ 172.2, 169.0, 157.0, 156.6, 151.3, 143.5, 140.9, 140.3, 137.3, 135.4, 134.6, 133.2, 130.0, 129.2, 126.4, 126.0, 125.9, 125.0, 123.3, 123.2, 122.0, 120.1, 118.6, 117.9, 116.2, 113.0, 112.0, 110.1,

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109.8, 105.7, 35.4, 31.4, MS (HR-FAB+) m/z: Found 702.3232 [(M+H)⁺]; Calculated for C₄₈H₃₉N₅O, View Article Online DOI: 10.1039/C9TC01354G

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalonitrile

5-Bromoisophthalonitrile (5.00 g, 24.15 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2dioxaborolane) (9.20 g, 36.23 mmol), potassium acetate (7.11g, 72.45 mmol) and [1,1'bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.53 g, 0.72 mmol) were poured into a 2-neck round-bottom flask. Then 1,4-dioxane (50 ml) was injected into mixture. The reaction was proceeded at reflux condition for 3 h. After the reaction, the reaction solution was filtered with celite and silica gel. Then the filtered solution was concentrated and adsorbed into silica gel. The adsorbed crude product was purified with column chromatography using a mixed eluent (methylene chloride: n-hexane=1:4) A white powder was obtained after purification (4.70 g, Yield 77%).

¹H NMR (500 MHz, CDCl₃) : δ 8.28 (s, 2H), 7.99 (s, 1H), 1.26 (s, 12H), MS (APCI) m/z: Found 254.8 [(M+H)⁺]; Calculated for C₁₄H₁₅BN₂O₂, 254.09

5-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)isophthalonitrile

2,4-Bis(4-(tert-butyl)phenyl)-6-chloro-1,3,5-triazine (3.08 g, 8.10 mmol) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalonitrile (2.47 g, 9.72 mmol) were dissolved in tetrahydrofuran solvent (60 ml) and directly poured into a 2-neck round-bottom flask. 2M aqueous potassium carbonate solution (30 ml) was injected into the mixed solution. Then tetrakis(triphenylphosphine) palladium(0) (0.28 g, 0.24 mmol) was poured into the reaction mixture. The reaction mixture was stirred and heated at reflux condition for 12 h. After cooling down to room temperature, the reaction mixture was filtered. A white powder was obtained after all purification. (2.10 g, Yield 56%)

¹H NMR (500 MHz, CDCl₃) : δ 9.17 (s, 2H), 8.61(d, 4H, J=8.5 Hz), 8.07 (s, 1H), 7.62 (d, 4H, J=8.0 Hz), 1.43 (s, 18H), MS (APCI) m/z: Found 472.2 [(M+H)⁺]; Calculated for C₃₁H₂₉N₅, 471.60

5-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)-2-bromoisophthalonitrile

5-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)isophthalonitrile (2.30 g, 4.88 mmol) was poured into a 2-neck round-bottomed flask and connected with a vacuum pump to remove residue solvent and moisture for 24 h. Then the round-bottomed flask was maintained under nitrogen. After that, the distilled tetrahydrofuran (100 ml) was injected to dissolve starting materials. Then the reaction solution was cooled down to -98°C using n-hexane/liquid nitrogen bath. After cooling for 2 h, lithium diisopropylamide (3.70 ml, 7.32 mmol) was dropped into reaction solution very slowly. Then, the lithiation was proceeded for 10 min and 1,2-dibromotetrachloroethane (3.18 g, 9.75 mmol) dissolved in distilled tetrahydrofuran (10 ml) was directly injected into the reaction mixture. Then the reaction was carried out at the low temperature for 12 h and room temperature for additional 12 h. After that, the reaction mixture was filtered. An ivory-white product was obtained after all purification. (1.35 g, Yield 49%).

¹H NMR (500 MHz, CDCl₃) : δ 9.17 (s, 2H), 8.64 (d, 4H, J=8.5 Hz), 7.63 (d, 4H, J=8.5 Hz), 1.42 (s, 18H), MS (APCI) m/z: Found 550.1 [(M+H)⁺]; Calculated for C₃₁H₂₈BrN₅, 550.49

2-(5H-benzofuro[3,2-c]carbazol-5-yl)-5-(4,6-bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-

yl)isophthalonitrile (Trz2CNBFCz)

5-(4,6-Bis(4-(tert-butyl)phenyl)-1,3,5-triazin-2-yl)-2-bromoisophthalonitrile (0.70 g, 1.27 mmol), 5Hbenzofuro[3,2-c]carbazole (0.36 g, 1.40 mmol), copper iodide (0.12 g, 0.64 mmol), and potassiumcarbonate (0.53 g, 3.81 mmol) were added into a pressure tube. Then DMF (10 ml) was added into the $mixture. After that, (<math>\pm$)-trans-1,2-diaminocyclohexane (0.10 ml, 0.64 mmol) was injected and the reaction mixed was stirred under heating to 120°C for 2 h. After end of reaction, the reaction mixture was cooled down to room temperature and extracted using methylene chloride. The extracted organic layer was filtered with celite/silica gel and concentrated using a rotary evaporator. Concentrated crude product was adsorbed into a silica gel and the adsorbed crude product was purified using column chromatography using a mixed eluent (methylene chloride: n-hexane=1:1). After column purification,

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the final product was further purified using a vacuum train sublimation. After all purification, a bright View Article Online DOI: 10.1039/C9TC01354G

¹H NMR (500 MHz, CDCl₃) : : δ 9.51 (s, 2H), 8.71 (d, 4H, J=8.5 Hz), 8.63 (d, 1H, J=7.0 Hz), 8.05 (d, 1H, J=8.5 Hz), 8.00 (d, 1H, J=7.5 Hz), 7.77 (d, 1H, J=8.0 Hz), 7.66 (d, 4H, J=8.5 Hz), 7.58-7.53 (m, 2H), 7.49 (t, 1H, J=7.75 Hz), 7.41 (t, 1H, J=7.25 Hz), 7.25-7.24 (m, 1H) , 7.17 (d, 1H, J=8.5 Hz), 1.43 (s, 18H), ¹³C NMR (125 MHz, CDCl₃) : δ 172.6, 167.5, 157.5, 156.8, 151.3, 145.5, 140.5, 139.9, 138.8, 138.5, 132.7, 129.3, 126.8, 126.2, 124.9, 123.7, 123.3, 122.8, 122.5, 120.3, 119.0, 118.8, 116.1, 114.4, 112.1, 110.4, 109.8, 105.3, 35.5, 31.4, MS (HR-FAB+) m/z: Found 727.3185 [(M+H)⁺]; Calculated for C₄₉H₃₈N₆O, 726.8656

Device Fabrication and measurements

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All of organic compounds were deposited on pattered indium tin oxide (ITO) substrate. All of TADF device structures were the same except for the emission layer (EML).

ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/EML (25 nm)/TSPO1 (5 nm)/TPBi

(20 nm)/LiF (1.5 nm)/Al (200 nm)

The hole injection layer was poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). The hole transport layer was 4,4'-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine] (TAPC). 1,3-Di(9H-carbazol-9-yl)benzene (mCP) was used for blocking triplet excitons in the EML. The EML consisted of (oxybis(2,1-phenylene))bis(diphenylphosphine oxide) (DPEPO) host and TrzBFCz or TrzCNBFCz or Trz2CNBFCz emitter. The doping concentration of each emitter was from 10 wt% to 30 wt%. Electron type exciton blocking layer was diphenyl(4-(triphenylsilyl)phenyl)phosphine oxide (TSPO1). 1,3,5-Tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TPBi) was used as an electron transport layer. All of fabricated devices were analyzed by using 2400 source measurement unit and CS 2000 spectroradiometer.

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