Accepted Manuscript

Effect of increasing electron donor units for high-efficiency blue thermally activated delayed fluorescence

Jae-Ryung Cha, Chil-Won Lee, Myoung-Seon Gong

PII: S0143-7208(16)31482-6

DOI: 10.1016/j.dyepig.2017.01.053

Reference: DYPI 5753

To appear in: Dyes and Pigments

Received Date: 26 December 2016

Revised Date: 20 January 2017

Accepted Date: 20 January 2017

Please cite this article as: Cha J-R, Lee C-W, Gong M-S, Effect of increasing electron donor units for high-efficiency blue thermally activated delayed fluorescence, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.01.053.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Graphical Abstract



Effect of increasing electron donor units for high-efficiency blue thermally activated delayed fluorescence

Jae-Ryung Cha^a, Chil-Won Lee^b, and Myoung-Seon Gong^{a,*}

^aDepartment of Nanobiomedical Science and BK21 PLUS NBM Global Research Center, Dankook University, Cheonan 31116, Republic of Korea

^bDepartment of Chemistry, Dankook University, Cheonan 31116, Republic of Korea

* Corresponding author. Tel.: +82 41 5501476; fax: +82 41 5503431.

E-mail: msgong@dankook.ac.kr (M. S. Gong)

ABSTRACT

To enhance the efficiency of organic light-emitting diodes (OLEDs), the application of triplet excitons must be maximized. Two donor–acceptor-type molecules bearing biscarbazolyl and tris-carbazolyl groups at the *ortho* position of a phenyl-attached triazine ring were synthesized. These molecules showed very small singlet–triplet energy gaps (ΔE_{ST}) of 0.06 and 0.03 eV, respectively, and transient photoluminescence (PL) characteristics, which indicate that they are thermally activated delayed fluorescence (TADF) materials. A high external quantum efficiency (EQE) of 16.5% with deep blue color coordinates of (0.15, 0.22) was observed using a TrisCz–Trz TADF emitter. This interaction between the electron donor and electron acceptor substituents plays a key role in achieving a very small ΔE_{ST} and good intramolecular charge transfer (ICT) activities with high photoluminescence (PL).

Keywords: TADF; OLED; Sky blue; Carbazole; Triazine; Blue dopant

1. Introduction

To date, the development of organic light-emitting diodes (OLEDs) has mainly focused on enhancing the operational lifetime and power consumption of devices to improve their overall efficiency. Commercialized OLED panels use phosphorescent materials with an internal quantum efficiency of 100% as their green and red light emitters. However, blue phosphorescent materials have a very short lifetime because of their relatively low molecular stability and high operation voltage in blue OLED devices. Therefore, a new methodology is required to achieve a high electroluminescent efficiency for blue OLED devices.

Recently, highly efficient fluorescent materials with high external quantum efficiencies have received increased attention owing to the use of thermally activated delayed fluorescence (TADF) emitters [1-9]. By combining the molecular structures of electron donors and electron acceptors, the energy difference between the singlet and triplet excited states (ΔE_{ST}) can be minimized to develop highly efficient TADF materials [9-13]. TADF phenomena are processes which apply thermal energy (approximately 28 meV) at room temperature to materials having an extremely small energy difference between the singlet and triplet states via the reverse intersystem crossing (RISC), where a triplet state passes to a more excited singlet state. TADF emitters which use singlet and triplet excitons can be exploited to enhance the external quantum efficiency and thus overcome the problems associated with traditional fluorescent materials.

To develop efficient TADF materials, the RISC and intramolecular charge transfer (ICT) need to occur efficiently. To enhance the RISC process, a smaller gap between the S_1 and T_1 energy levels is desirable. However, when the electronic distributions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) overlap, the S1 energy level increases as a result. Therefore, the electron density overlap of the HOMO and LUMO levels needs to be minimized. To prevent electron density overlap, twisted molecular structures are preferred [14]. There is a trade-off between the RISC efficiency and the ICT efficiency. Therefore, the overlap of the HOMO and LUMO distributions needs to be adequately adjusted. Carbazole derivatives with a stable structure have been used as electron donor moieties of TADF emitters [15-23]. Because carbazole consists only of aromatic moieties; thus, it has a high bond dissociation energy. Triazine derivatives have also proven to be stable because of their aromatic character. Therefore, TADF emitters have been developed using carbazole (electron donor moiety) and triazine (electron acceptor moiety) [23-30]. However, the TADF materials reported to date have a severe efficiency roll-off at a high luminance owing to triplet-triplet annihilation and the triplet-polaron quenching effect [31].

In this work, we designed and synthesized donor–acceptor-type molecules [9,9'-((6phenyl-1,3,5-triazine-2,4-diyl)bis(2,1-phenylene))bis(9*H*-carbazole) (**BisCz–Trz**) and 2,4,6-tris(2-(9*H*-carbazol-9-yl)phenyl)-1,3,5-triazine (**TrisCz–Trz**)] for application as blue TADF emitters in OLEDs. In these molecules, two and three carbazole electron donor units are introduced at the *ortho* position of the phenyl ring of the triazine electron acceptor. These molecules exhibit a very small ΔE_{ST} (0.03–0.06 eV) with very high electroluminescence efficiencies. Optimized blue TADF devices using **TrisCz-Trz**

3

show a maximum quantum efficiency of 16.5% and chromaticity coordinates (0.15, 0.22) in the deep blue range. Moreover, the roll-off at 100–1000 cd/m² is less than 10% (16.5% \rightarrow 15.6%; 5.45% efficiency drop compared to the maximum efficiency), meaning that the quantum efficiency drop phenomena have been greatly improved in the high luminescence range compared to existing blue TADF materials.

2. Experimental

2.1. Materials and Measurements.

Zinc chloride, 9*H*-carbazole, 1,2-dibromobenzene, copper iodide (Aldrich Chem. Co.), 1,1'-bis(diphenylphosphino)ferrocene-palladium(II) dichloride dichloromethane complex, tetrakis(triphenylphosphine)palladium(0), 2,4-dichloro-6-phenyl-1,3,5-triazine, 2,4,6-trichloro-1,3,5-triazine, and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (P&H Tech. Co. Korea) were used without further purification. Potassium carbonate, potassium acetate, *N*,*N*-dimethylacetamide, 1,4-dioxane, tetrahydrofuran, dichloromethane, n-hexane, and nitromethane (DukSan Sci. Co. Korea) were used as received.

The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded using a Varian Ascend 500 (500 MHz) spectrometer. The photoluminescence (PL) spectra were fluorescence spectrophotometer recorded using (Jasco FP-6500), and а photoluminescence quantum yield (PLQY) was measured by absolute PL quantum yield spectrometer (Hamamatsu, C11347-11). Ultraviolet-visible (UV-vis) spectra were obtained by means of a UV-vis spectrophotometer (Shimadzu UV-1601PC). Elemental analyses (EAs) were performed using a Thermo Fisher Scientific Flash 2000 elemental analyser, and low- and high-resolution mass spectra were recorded using a JEOL JMS-600W spectrometer in the electron ionization (EI) and fast atom bombardment (FAB) modes. Differential scanning calorimetry (DSC) measurements were performed using a Shimadzu DSC-60 calorimeter in nitrogen at a heating rate of 10 °C/min, and the thermogravimetric analysis (TGA) measurements were performed using a Shimadzu TGA-50 thermogravimetric analyser at a heating rate of 10 °C /min.

2.2. Preparation of 9-(2-bromophenyl)-9H-carbazole

A mixture of 9*H*-carbazole (5.5 g, 32.89 mmol), 1,2-dibromobenzene (11.64 g, 49.34 mmol), copper iodide (3.13 g, 16.45 mmol), and potassium carbonate (9.09 g, 65.79 mmol) in anhydrous *N*,*N*-dimethylacetamide (120 mL) was degassed with nitrogen for 30 min while stirring. The reaction mixture was then refluxed in nitrogen for 24 h. The crude mixture was filtered, and the residue was washed with dichloromethane (3×50 mL). The combined filtrates were evaporated until they were dry The residue was purified by column chromatography (silica gel, 50% *n*-hexane in dichloromethane) to give 9-(2-bromophenyl)-9*H*-carbazole as a white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.06 (d, 2H, *J* = 12 Hz), 7.28 (t, 2H, *J* = 18 Hz), 7.39 (t, 3H, *J* = 18 Hz), 7.43-7.52 (m, 2H), 7.84 (d, 1H, *J* = 12 Hz), 8.14 (d, 2H, *J* = 12 Hz). ¹³C NMR (CDCl₃): δ 110.0, 120.0, 120.3, 123.2, 123.8, 125.9, 128.8, 130.1, 131.1, 134.2, 136.7, 140.8.

2.3. Preparation of 9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9Hcarbazole

A mixture of 9-(2-bromophenyl)-9*H*-carbazole (10 g, 31.04 mmol), 4,4,4',4',5,5,5',5'octamethyl-2,2'-bi(1,3,2-dioxaborolane) (10.25 g, 40.35 mmol), 1,1'bis(diphenylphosphino)ferrocene-palladium(II) dichloride dichloromethane complex (0.76 g, 0.93 mmol), potassium acetate (9.14 g, 93.11 mmol), and anhydrous 1,4dioxane (180 ml) was degassed with nitrogen for 1 h while stirring. The reaction mixture was then maintained in nitrogen at 80 °C for 24 h. The mixture was diluted with dichloromethane and washed with distilled water (100 mL) three times. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo* to give the crude product, which was purified by column chromatography using dichloromethane/*n*- hexane and gave a white powder.

¹H NMR (500 MHz, CDCl₃): δ 0.79 (s, 12H), 7.18 (d, 2H, *J* = 12 Hz), 7.25 (t, 2H, *J* = 18 Hz), 7.37 (t, 2H, *J* = 18 Hz), 7.53 (t, 2H, *J* = 18 Hz), 7.69 (t, 1H, *J* = 16 Hz), 7.96 (d, 1H, *J* = 12 Hz), 8.14 (d, 2H, *J* = 12 Hz). ¹³C NMR (CDCl₃): δ 24.4, 83.4, 109.7, 119.1, 119.9, 123.1, 125.5, 127.6, 128.6, 132.1, 136.3, 142.1, 142.4.

2.4. Preparation of 9,9'-((6-Phenyl-1,3,5-triazine-2,4-diyl)bis(2,1-phenylene))bis(9H-carbazole) (**BisCz-Trz**)

9-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (11.04 g, 27.87 mmol), 2,4-dichloro-6-phenyl-1,3,5-triazine (3 g, 13.27 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.53 g, 1.33 mmol) were dissolved in a 2 M potassium carbonate solution (40 mL) and tetrahydrofuran (100 mL). The reaction mixture was stirred for 24 h at 80 °C. The mixture was diluted with dichloromethane and washed with distilled water (100 mL) three times. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo* to give the crude product, which was purified by column chromatography using dichloromethane/*n*-hexane and gave a pale yellow powder.

BisCz-Trz: Yield 71%. T_g : 100 °C, T_m : 263 °C, T_d : 374 °C (5% weight loss). ¹H NMR (500 MHz, CDCl₃): δ 6.79 (d, 2H, J = 8 Hz), 6.895 (t, 2H, J = 15 Hz), 6.965 (d, 4H, J = 8 Hz), 7.163–7.217 (m, 5H), 7.263 (t, 4H, J = 15 Hz), 7.478 (t, 2H, J = 15 Hz), 7.563 (d, 2H, J = 8 Hz), 7.659–7.708 (m, 4H), 7.986 (d, 4H, J = 8Hz). ¹³C NMR (CDCl₃): δ 109.4, 119.4, 120.1, 123.3, 125.9, 127.8, 128.4, 128.6, 130.4, 131.9, 132.4, 132.6, 135.3, 136.4, 141.5. Mass (EI⁺) m/z 639 [(M+H)⁺]. Anal Calcd for C₄₅H₂₉N₅: C, 84.48%; H, 4.57%; N, 10.95%. Found: C, 84.48%; H, 4.57%; N, 10.86%. UV-vis: λ_{max}

= 339 (THF) nm. Fluorescence: λ_{max} (emission) = 457 (solid state) nm. $\Phi_{\text{fl}} = 0.756$.

2.5. Preparation of 2,4,6-Tris(2-(9H-carbazol-9-yl)phenyl)-1,3,5-triazine (TrisCz-Trz) 9-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (15.36)g, 53.68 mmol), 2,4,6-trichloro-6-1,3,5-triazine (3 16.27 mmol), g, and tetrakis(triphenylphosphine)palladium(0) (2.82 g, 2.44 mmol) were dissolved in a 2 M potassium carbonate solution (40 mL) and tetrahydrofuran (100 mL). The reaction mixture was stirred for 24 h at 80 °C. The mixture was diluted with dichloromethane and washed with distilled water (100 mL) three times. The organic layer was dried over anhydrous MgSO₄ and evaporated *in vacuo* to give the crude product, which was purified by column chromatography using dichloromethane/*n*-hexane and gave a pale yellow powder.

TrisCz-Trz: Yield 37%. T_g: 126 °C, T_m: 323 °C, T_d: 395 °C (5% weight loss). ¹H NMR (500 MHz, CDCl₃): δ 6.238 (d, 3H, J = 8 Hz), 6.558 (d, 6H, J = 8 Hz), 6.968 (t, 3H, J = 15 Hz), 7.216–7.261 (m, 12H), 7.341 (d, 3H, J = 8 Hz), 7.485 (t, 3H, J = 15 Hz), 8.100 (d, 6H, J = 7 Hz). ¹³C NMR (CDCl₃): δ 109.4, 119.2, 123.2, 125.9, 128.2, 130.0, 132.2, 133.6, 136.0, 141.3, 170.2. Mass (EI⁺) m/z 803 [(M+H)⁺]. Anal Calcd for C₅₇H₃₆N₆ C, 85.05%; H, 4.51%; N, 10.44%. Found: C, 85.07%; H, 4.49%; N, 10.45%. UV-vis: $\lambda_{max} = 339$ (THF) nm. Fluorescence: λ_{max} (emission) = 457 (solid state) nm. Φ_{fl} = 0.708.

2.6. Device fabrication and measurements

All devices were basically prepared using a vacuum thermal evaporation process. 4,4'-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)aniline] (TAPC) was chosen as a hole transport layer; 1,3-bis(*N*-carbazolyl)benzene (mCP) and diphenylphosphine oxide-4(triphenylsilyl)phenyl (TSPO1) were applied as the exciton blocking and hole blocking layers; 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBi) was used as the electron transport layer; and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and *N*,*N*'-diphenyl-*N*,*N*'-bis-[4-phenyl-m-tolyl-amino]-phenyl]-biphenyl-4,4'-diamine (DNTPD) were used as the hole injection layer. The reason for using DNTPD instead of PEDOT-PSS is to adjust the charge injection and charge transfer for charge balance. Device structures for devices I, II, and III are as follows and are shown in **Fig. 1**.

<Fig. 1>

Device I: ITO/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/mCP:**BisCz-Trz** (25 nm, 1, 3, and 5% doping)/TSPO1 (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al (200 nm). Device II: ITO/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/mCP:**TrisCz-Trz** (25 nm, 1, 3, 7 and 10% doping)/TSPO1 (5 nm))/TPBi (30 nm)/LiF (1 nm)/Al (200 nm).

Device III: ITO/DNTPD (50 nm)/TAPC (20 nm)/mCP (10 nm)/mCP:**TrisCz-Trz** (25nm, 7% doping)/TSPO1 (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al (200 nm).

The electrical evaluation of the devices was performed with a Keithley 2400 sourcemeter, and the optical evaluation was carried out with CS 2000 spectroradiometer.

3. Results and discussion

3.1. Synthesis and characterization

The two TADF emitters developed in this work have two and three carbazole units as the electron donor moieties, and the triazine electron acceptor moiety is linked to the two- and three-carbazole moieties through a phenyl spacer at the *ortho* position. Scheme 1 presents the synthesis of the two blue TADF materials. **BisCz-Trz** and **TrisCz-Trz** were prepared by the Suzuki coupling reaction between the boronic ester form of alkylsubstituted 9-phenylcarbazole, 2,4-dichloro-6-phenyl-1,3,5-triazine, and 2,4,6-trichloro-6-1,3,5-triazine. **BisCz-Trz** and **TrisCz-Trz** purified by column chromatography and vacuum sublimation were used for material characterization and device fabrication.

Fig. 2 presents the molecular orbitals of the TADF emitter calculated by using the B3LYP 6-31G* basis set of the Gaussian 09 program. The HOMO was mainly located at the carbazole unit of the TADF emitters, and the LUMO was dispersed over the phenyl-spacer-triazine unit regardless of the type of electron donor moiety. The large torsion angles separating the HOMO and LUMO of **BisCz-Trz** and **TrisCz-Trz** were 66° and 67°, respectively. The *ortho* linkage can distort the carbazole from the phenyl plane by steric hindrance, and the degree of HOMO-LUMO overlap at the TADF emitter can be decreased by the large torsion angle between the electron donor and electron acceptor moiety.

<Fig. 2>

The Calculated ΔE_{ST} of **BisCz-Trz** and **TrisCz-Trz** was 0.06 and 0.04 eV, respectively, and was expected to cause an RISC. Moreover, the HOMO and LUMO are not completely separated but adequately separated. It is expected that the fluorescence

quantum efficiency, because the partially overlapping HOMO and LUMO in the phenyl spacer improves the ICT characteristics.

3.2. Thermal properties

The thermal stability of **BisCz-Trz** and **TrisCz-Trz** was studied by using thermograms from DSC and TGA. The glass transition temperature T_g was determined from the inflection point of the endothermic curves: 100 °C for **BisCz-Trz** and 126 °C for **TrisCz-Trz**. The value of T_g was 26 °C higher for **TrisCz-Trz** compared to **BisCz-Trz** because the former has a symmetric structure and high molecular weight. The melting points of **BisCz-Trz** and **TrisCz-Trz** were 263 and 323 °C, respectively. From the TGA measurements, we determined the 5% weight loss temperature to be 374 °C for **BisCz-Trz** and 395 °C for **TrisCz-Trz** (**ESI Fig. S5-S6**). **BisCz-Trz** and **TrisCz-Trz** have high thermal stability, which is expected to show favorable properties for device stability and lifetime.

3.3. Optical properties

The light absorption and emission of the blue TADF materials were analysed by using UV-vis and PL spectroscopy. **Fig. 3** presents the UV-vis absorption and PL spectra of **BisCz-Trz** and **TrisCz-Trz**. The 290–300 nm range is the π - π * transition; the 300–350 nm range is the n- π * transition of carbazole; and the 350–450 nm range shows the ICT absorption characteristics between electron accepter unit (triazine moiety) and electron donor unit (carbazole moiety). This type of absorption occurs more strongly in **TrizCz-Trz** where the electron donor unit is increased. The measurement of the singlet energy of **BisCz-Trz** and **TrisCz-Trz** was determined in the maximum emission wavelength of

PL in polystyrene matrix, which was measured the same at 2.71 eV (PL_{max} 457 nm.)

The triplet energies of **BisCz-Trz** and **TrisCz-Trz** were 2.65 and 2.68 eV, respectively, on the basis of the phosphorescent emission peak in a frozen tetrahydrofuran solution measured at 77 K after a delay time of 100 μ s was applied. The singlet–triplet energy gaps (ΔE_{ST}) of **BisCz-Trz** and **TrisCz-Trz** were 0.06 and 0.03 eV, respectively. **BisCz-Trz** and **TrisCz-Trz** emitters designed on the basis of the *ortho*-phenyl linkage platform exhibited a very small ΔE_{ST} less than 0.1 eV via the distortion of the molecular geometry. The singlet and triplet energies of the TADF emitters were reduced by modifying the number of carbazole moieties as the electron donor group.

<Fig. 3>

The decay curves of the delayed fluorescence emissions of **BisCz-Trz** and **TrisCz-Trz Trz** were investigated by transient PL measurements of **BisCz-Trz** and **TrisCz-Trz** dispersed in mCP. **Fig. 4** shows the transient PL decay curves of **BisCz-Trz** and **TrisCz-Trz**. The lifetimes of the delayed emission calculated from the decay curves were 5.4 μ s for **BisCz-Trz** and 5.0 μ s for **TrisCz-Trz**. This indicates that the delayed fluorescence process contributes to the light emissions of **BisCz-Trz** and **TrisCz-Trz**. The reason for the relatively short decay time is that the effective RISC occurs as a result of the small singlet–triplet energy difference; therefore, the concentration of the triplet-state excitons is rapidly exhausted.

<Fig. 4>

3.4. Electrochemical properties

The ionization potential (IP) and electron affinity (EA) of the blue TADF emitters were measured by cyclic voltammetry (CV) to predict the HOMO and LUMO, as shown **Fig. 5**. The IP/EA of **BisCz-Trz** and **TrisCz-Trz** were -6.10/-3.35 eV and -6.11/-3.33 eV, respectively. The IP/EA gaps were 2.75 and 2.78 eV for **BisCz-Trz** and **TrisCz-Trz**, respectively. The HOMO/LUMO levels were similar in the **BisCz-Trz** and **TrisCz-Trz** emitters. These results show similar LUMO levels, despite the increased carbazole unit because the interaction between the carbazole and triazine units also minimizes the influence on triazine. **Table 1** presents the basic thermal and photophysical properties of **BisCz-Trz** and **TrisCz-Trz**.

<Fig. 5> <Table. 1>

3. 5. Device properties

The two TADF emitters were evaluated as blue emitters by doping in the mCP host material. **Fig. 6** shows the current-density–voltage and luminance–voltage curves of devices I, II, and III. The decrease in the current density of device II for the increase from 1% doping to 3% or 7% doping is due to the charge (electron) trapping effect of the TADF materials in the LUMO level. The decrease in the current density when the dopant concentration is changed from 7% to 10% is due to the increase in charge transfer between dopants.

<Fig. 6>

The quantum efficiencies of devices I, II, and III were calculated from the current density and luminance are plotted versus the luminance in **Fig. 7**. The increase in the number of electron donor units enhanced the external quantum efficiency (EQE). The maximum EQEs of devices I (3%), II (7%), and III (7%) were 12.2%, 14.9%, and 16.5%, respectively. A dramatic improvement in the EQE was realized by increasing the number of carbazole units attached to the *ortho*-phenyl linkage. The EQE decreased slowly with increasing luminance and the EQE of device III remained 16.5% at 100

 cd/m^2 and 15.6% at 1000 cd/m^2 , corresponding to 100% and 94.5% of the maximum EQE, respectively.

The triplet energy difference between mCP of host material and BisCz-Trz or TrisCz-Trz was less than 0.3 eV. Triplet excitons formed in the light emitting layer mainly remained stayed in dopants, thus the dopant-dopant TTA was caused because of a long lifetime relative to the singlet excitons. Generally, TTA can be explained by the Dexter or Förster transfer mechanism, when two triplet excitons are in close proximity. Through this energy transfer process, one is formed in a high energy state (T_n or S_n) and the other is formed in the bottom energy state (S_o) [32]. If the concentration of the dopant is high or if the dopant is aggregated, the triplet excitons can cause TTA through Dexter energy transfer in principle. An exchange of electrons occurred through overlap of Dexter energy transfer molecular orbital, and the S_o state and T_n or S_n state are formed through electron transfer of HOMO \rightarrow HOMO and LUMO \rightarrow LUMO.

In the molecular structure of TrisCz-Trz, the acceptor unit of triazine is surrounded by a donor unit in the carbazole. Therefore, HOMO and LUMO is located outside and inside of the molecular, so that the overlap of LOMO between two triplet excitons become limited. As a result, in order to generate TTA by the Dexter mechanism, both HOMO and LUMO electrons must be able to move. However, in the case of TrisCz-Trz, the transfer of LUMO electrons is limited and the TTA phenomenon is expected to be reduced. Due to these molecular structural properties, the roll-off properties of TTA in the device are improved compared to other TADF materials.

 Table 2 presents the characteristics of devices I, II, and III at different doping concentrations.

Fig. 8 presents the electroluminescence (EL) spectra of **BisCz-Trz** and **TrisCz-Trz** devices characterized with a spectroradiometer. The maximum emission peaks of devices I, II, and III were 465, 467, and 468 nm, respectively, and very similar characteristics were obtained. The full width at half maximum (FWHM) values of devices I, II, and III were 63, 62, and 64 nm, respectively. The color coordinates of devices I, II, and III were (0.15, 0.20), (0.15, 0.21) and (0.15, 0.22) respectively. Although the number of carbazole units increased, devices I, II, and III had similar color coordinates and maximum emission wavelengths with a narrow emission spectrum.

<Fig. 8>

4. Conclusion

In conclusion, new blue TADF emitters, **BisCz-Trz** and **TrisCz-Trz**, were designed and synthesized. These molecules demonstrated very small ΔE_{ST} (0.03–0.06 eV) and improved ICT characteristics by increasing the number of electron donor units and *ortho*-linking electron donor and electron acceptor moieties. The blue TADF device using **TrisCz-Trz** showed a high quantum efficiency and deep blue emission in the high luminescence range (100–1000 cd/m²). Therefore, the *ortho*-linked design approach can be useful for TADF material design to obtain a small ΔE_{ST} and good ICT transition. A molecular design strategy which includes more electron donor units and distributes the HOMO uniformly would allow for the development of high-EQE TADF devices.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2013R1A1A2011560) the MOTIE (Ministry of Trade, Industry & Energy (project number 10051350)) and KDRC (Korea Display Research Consortium) support program for the development of future devices technology for display industry.

References

- Goushi K, Yoshida K, Sato K, Adachi C. Organic light-emitting diodes employing efficient reverse intersystem crossing for triplet-to-singlet state conversion. Nat Photonics 2012;6:253-258.
- Lee DR, Kim M, Jeon SK, Hwang S-H, Lee CW, Lee JY. Design strategy for 25% external quantum efficiency in green and blue thermally activated delayed fluorescent devices. Adv Mater 2015;27:5861-5867.
- Fan C, Duan C, Wei Y, Ding D, Xu H, Huang W. Dibenzothiophene-based phosphine oxide host and electron-transporting materials for efficient blue thermally activated delayed fluorescence diodes through compatibility optimization. Chem Mater 2015;27:5131-5140.
- Hofbeck T, Monkowius U, Yersin H. Highly efficient luminescence of Cu(I) compounds: thermally activated delayed fluorescence combined with short lived phosphorescence. J Am Chem Soc 2015;137:399-404.
- Hu J, Li Y, Zhu H, Qiu S, He G, Zhu X, et al. Photophysical properties of intramolecular charge transfer in a tribranched donor-π-acceptor chromophore. Chem Phys Chem 2015;16:2357-2365.
- 6. Sagara Y, Shizu K, Tanaka H, Miyazaki H, Goushi K, Kaji H, et al. Highly efficient thermally activated delayed fluorescence emitters with a small singlet-triplet energy gap and large oscillator strength. Chem Lett 2015;44:360-362.
- Sun JW, Baek JY, Kim K-H, Moon C-K, Lee J-H, Kwon S-K, et al. Thermally activated delayed fluorescence from azasiline based intramolecular chargetransfer emitter (DTPDDA) and a highly efficient blue light emitting diode. Chem Mater 2015;27:6675-6681.

- Wang H, Meng L, Shen X, Wei X, Zheng X, Lv X, et al. Highly efficient orange and red phosphorescent organic light-emitting diodes with low roll-off of efficiency using a novel thermally activated delayed fluorescence material as host. Adv Mater 2015;27:4041-4047.
- Hirata S, Sakai Y, Masui K, Tanaka H, Lee SY, Nomura H, et al. Highly efficient blue electroluminescence based on thermally activated delayed fluorescence. Nat Mater 2015;14:330-336.
- 10. Lee J, Shizu K, Tanaka H, Nomura H, Yasuda T, Adachi C. Oxadiazole- and triazole-based highly-efficient thermally activated delayed fluorescence emitters for organic light-emitting diodes. J Mater Chem C 2013;1:4599-4604.
- 11. Tao Y, Yuan K, Chen T, Xu P, Li H, Chen R, et al. Thermally activated delayed fluorescence materials towards the breakthrough of organoelectronics. Adv Mater 2014;26:7931-7958.
- 12. Zhang Q, Li B, Huang S, Nomura H, Tanaka H, Adachi C. Organic light emitting diodes: phosphorescence meets its match. Nat Photonics 2014;8:269-270.
- 13. Uoyama H, Goushi K, Shizu K, Nomura H, Adachi C. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 2012;492:234-238.
- 14. Shizu K, Noda H, Tanaka H, Taneda M, Uejima M, Sato T, Tanaka K, Kaji H, Adachi C. Highly efficient blue electroluminescence using delayed-fluorescence emitters with large overlap density between luminescent and ground states. J Phys Chem C 2015;119:26283-26289.
- 15. Zhang Q, Li J, Shizu K, Huang S, Hirata S, Miyazaki H, Adachi C. Design of efficient thermally activated delayed fluorescence materials for pure blue organic light emitting diodes. J Am Chem Soc 2012;134:14706-14709.

- 16. Masui K, Nakanotani H, Adachi C. Analysis of exciton annihilation in highefficiency sky-blue organic light-emitting diodes with thermally activated delayed fluorescence. Org Electron 2013;14:2721–2726.
- 17. Lee S-Y. Yasuda T, Yang Y-S, Zhang Q, Adachi C. Luminous butterflies: efficient exciton harvesting by benzophenone derivatives for full-color delayed fluorescence OLEDs. Angew Chem Int Ed 2014;53:6402–6406.
- 18. Cho Y-J, Yook K-S, Lee J-Y. High efficiency in a solution processed thermally activated delayed-fluorescence device using a delayed-fluorescence emitting material with improved solubility. Adv Mater 2014;26:6642–6646.
- 19. Tang C, Yang T, Cao X, Tao Y, Wang F, Zhong C, Qian Y, Zhang X, Huang W. Tuning a weak emissive blue host to highly efficient green dopant by a CN in tetracarbazolepyridines for solution processed thermally activated delayed fluorescence devices. Adv Opt Mater 2015;3:786–790.
- 20. Cho Y-J, Jeon S-K, Chin B-D, Yu E, Lee J-Y. The design of dual emitting cores for green thermally activated delayed fluorescent materials. Angew Chem Int Ed 2015;54:5201-5204.
- 21. Kim M, Jeon S-K, Hwang S, Lee J-Y. Stable blue thermally activated delayed fluorescent organic light-emitting diodes with three times longer lifetime than phosphorescent organic light-emitting diodes. Adv Mater 2015;27:2515–2520.
- 22. Huang B, Qi Q, Jiang W, Tang J, Liu Y, Fan W, Yin Z, Shi F, Ban X, Xu H, Sun Y. Thermally activated delayed fluorescence materials based on 3,6-di-tert-butyl-9-((phenylsulfonyl)phenyl)-9H-carbazoles. Dyes Pigm 2014;111:135-144.
- 23. Albrecht K, Matsuoka K, Fujita K and Yamamoto K. Carbazole Dendrimers as solution-processable thermally activated delayed-fluorescence materials. Angew

Chem Int Ed 2015;54:5677-5682.

- 24. Endo A, Sato K, Yoshimura K, Kai T, Kawada A, Miyazaki H, Adachi C. Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes. Appl Phys Lett 2011;98:083302.
- 25. Adachi C. Third-generation organic electroluminescence materials. J Appl Phys 2014;53:060101.
- 26. Lee SY, Yasuda T, Nomura H, Adachi C. High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules. Appl Phys Lett 2012;101:093306.
- 27. Sato K, Shizu K, Yoshimura K, Kawada A, Miyazaki H, Adachi C. Organic luminescent molecule with energetically equivalent singlet and triplet excited states for organic light-emitting diodes. Phys Rev Lett 2013;110:247401.
- 28. Serevicius T, Nakagawa T, Kuo MC, Cheng SH, Tseng MR, Yasuda T, Adachi C. Enhanced electroluminescence based on thermally activated delayed fluorescence from a carbazole–triazine derivative. Phys Chem Chem Phys 2013;15:15850-15855.
- 29. Shizu K, Sakai Y, Tanaka H, Hirata S, Adachi C, Kaji H. Meta-linking strategy for thermally activated delayed fluorescence emitters with a small singlet-triplet energy gap. Phys Chem Chem Phys 2015;3:108-113.
- 30. Jeon SK, Yook KS, Lee JY. Highly efficient exciplex organic light-emitting diodes using thermally activated delayed fluorescent emitters as donor and acceptor materials. Nanotechnology 2016;27:224001.
- 31. Lin T, Zhang T, Song Q, Jin F, Liu Z, Su Z, Luo Y, Chu B, Lee C. S. and Li W.

Thermally activated delayed-fluorescence organic light-emitting diodes based on exciplex emitter with high efficiency and low roll-off. Org Electron 2016;38:69-73.

 Murawski C, Leo K and Gather M. C. Efficiency roll-off in organic light-emitting diodes. Adv Mater 2013;25:6801-6827.

20

Table captions

Table 1. Basic thermal and photophysical properties of **BisCz-Trz** and **TrisCz-Trz**.**Table 2.** Blue TADF OLEDs characteristics using **BisCz-Trz** and **TrisCs-Trz** at differentdoping concentrations.

PropertiesBisC2-IFZTrisC2-IFZ"HighesPurityHPLC%99.999.9occupieThermalDSC T_g 100126dAnalysis(°C) T_m 263323moleculUVMax(nm)339339arOpticalPL(Solid) S_1 2.71 (457 nm)2.71 (457 nm)AnalysisLT PL T_1 2.652.68a)LowesElectricalCV(eV)HOMO ^a -6.10-6.11unoccupAnalysisCV(eV)HUMO ^b iedied			Materials	DiaCa Taa		```
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Properties			DISCZ-11Z	TrisCz-Trz	^{a)} Highes
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Purity	HPLC	%	99.9	99.9	occupie
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Thermal	DSC	T_g	100	126	d
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Analysis	(°C)	T_m	263	323	molecul
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		UV	Max(nm)	339	339	ar
AnalysisLT PL T_1 2.652.68a)LowesPLQY%75.670.8tElectrical Analysis $CV(eV)$ HOMOa-6.10-6.11ied	Optical	PL(Solid)	\mathbf{S}_1	2.71 (457 nm)	2.71 (457 nm)	orbital ^{a)} Lowes
PLQY%75.670.8tElectrical AnalysiaHOMO ^a -6.10-6.11ied	Analysis	LT PL	T_1	2.65	2.68	
Electrical CV(eV) HOMO ^a -6.10 -6.11 ied		PLQY	%	75.6	70.8	t
Analysis LUMO ^b	Electrical	CV(eV)	HOMO ^a	-6.10	-6.11	ied
Anarysis LOMO -3.35 -3.33 molecul	Analysis		LUMO ^b	-3.35	-3.33	molecul

Table 1. Basic thermal and photophysical properties of BisCz-Trz and TrisCz-Trz.

ar orbital.

	Maximum		500 cd m ⁻² (1000 cd m ⁻²)					
Devices	QE ^{a)}	PE ^{b)}	CE ^{c)}	QE	PE	CE	Voltage	Color
	[%]	[lm W ⁻¹]	[cd A ⁻¹]	[%]	[lm W ⁻¹]	[cd A ⁻¹]	[V]	coordinate
BisCz-Trz 1%	4.2	2.7	6.3	3.2	1.7	4.9	9.1	0.18, 0.21
BisCz-Trz 3%	12.2	6.5	18.5	11.5 (8.9)	5.7 (4.2)	17.4 (13.5)	9.6 (8.9)	0.15, 0.20
BisCz-Trz 5%	10.9	6.4	16.7	8.4 (6.8)	4.2 (3.2)	12.9 (10.4)	9.7 (6.8)	0.15, 0.21
TrisCz-Trz 1%	8.8	7.3	12.8	7.0	4.3	10.2	7.5	0.15, 0.19
TrisCz-Trz 3%	11.1	8.2	17.0	8.2 (6.9)	4.3 (3.3)	12.6 (10.5)	9.2 (10.0)	0.15, 0.21
TrisCz-Trz 7%	14.9	9.6	23.0	14.7 (13.4)	8.4 (7.1)	22.8 (20.8)	8.5 (9.3)	0.15, 0.21
TrisCz-Trz 10%	11.3	8.5	18.3	10.6 (9.2)	6.8 (5.3)	17.2 (15.0)	8.0 (8.9)	0.15, 0.23
TrisCz-Trz 7% (DNTPD)	16.5	12.3	23.9	14.8 (15.6)	8.1 (9.3)	21.3 (22.5)	8.3 (7.7)	0.15, 0.22

Table 2. Blue TADF OLEDs characteristics using **BisCz-Trz** and **TrisCs-Trz** atdifferent doping concentrations.

^{a)}QE, quantum efficiency; ^{b)}PE, power efficiency; ^{c)}CE, current efficiency.

Scheme and Figure captions

Scheme 1. Synthetic scheme of BisCz-Trz and TrisCz-Trz.

Fig. 1. Device structure of the blue thermally activated delayed fluorescent device using BisCz-Trz and TrisCz-Trz.

Fig. 2. Simulated HOMO and LUMO distribution of BisCz-Trz and TrisCz-Trz.

Fig. 3. UV-vis solid PL and low temperature PL spectra of BisCz-Trz and TrisCz-Trz.

Fig. 4. Photoluminescence decay curves of BisCz-Trz and TrisCz-Trz.

Fig. 5. Electrochemical oxidation and reduction curves of BisCz-Trz and TrisCz-Trz.

Fig. 6. Current density-voltage and luminance-voltage curves of blue TADF OLEDs.

Fig. 7. Quantum efficiency-luminance curves of blue TADF OLEDs.

Fig. 8. EL spectra of blue TADF OLEDs.



Scheme 1. Synthetic scheme of BisCz-Trz and TrisCz-Trz.



Fig. 1. Device structure of the blue thermally activated delayed fluorescent device using

BisCz-Trz and TrisCz-Trz.



Fig. 2. Simulated HOMO and LUMO distribution of BisCz-Trz and TrisCz-Trz.



Fig. 3. UV-vis solid PL and low temperature PL spectra of BisCz-Trz and TrisCz-Trz.



Fig. 4. Photoluminescence decay curves of BisCz-Trz and TrisCz-Trz.



Fig. 5. Electrochemical oxidation and reduction curves of BisCz-Trz and TrisCz-Trz.



Fig. 6. Current density-voltage and luminance-voltage curves of blue TADF OLEDs.





Fig. 7. Quantum efficiency-luminance curves of blue TADF OLEDs.



Fig. 8. EL spectra of blue TADF OLEDs.

Highlights

•Two donor–acceptor molecules with carbazoles at the ortho position of a phenyltriazine ring were prepared.

- The two and three electron donor-acceptor-type TADF dopant materials were synthesized.
- Blue color coordinates of (0.15, 0.22) was observed using a TrisCz–Trz emitter.
- It showed high EQE of 16.5% and ΔE_{ST} of 0.03 eV.

1