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Author Statement

J. H. Maeng and D. K. wrote the manuscript. D. H. Ahn, H. Lee and Y. H. Jung measured and analyzed the photophysical, electrochemical and electroluminescence properties. J. Y. Lee and J. H. Maeng designed and synthesized the materials. D. H. Ahn, H. Lee and Y. H. Jung designed the optimized OLED configuration and fabricated all OLED devices. J. H. Kwon supervised this research. All authors contributed to the discussion of the results and to the writing of the manuscript.

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Rigid Indolocarbazole Donor Moiety for Highly Efficient Thermally Activated Delayed Fluorescent Device

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Abstract:

A new rigid donor moiety, namely, triphenyl-substituted indolocarbazole for thermally activated delayed fluorescence (TADF) materials is reported. Based on this donor, two novel TADF emitters 5-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-6,11,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TDBA-TPDICz) and 5-(4-(4,6diphenyl-1,3,5-triazin-2-yl)phenyl)-6,11,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TRZ-TPDICz) are synthesized and evaluated as TADF emitters. The phenyl substitutions at 6, 12-positions of donor moiety increase the steric hindrance between the donor and the acceptor resulting in increase in dihedral angle between them. As a consequence, the change in the TADF properties of these emitters are analyzed by photophysical, electrochemical properties and compared with the analogs reference material 5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-11-phenyl-5,11-dihydroindolo[3,2-b]carbazole (TRZ-pIC). Further, the TADF device fabricated with TDBA-TPDICz shows the deep blue color CIE coordinates of (0.14, 0.14) with a maximum external quantum efficiency (EQE) of 16.9 % and maximum current efficiency (CE) of 21.4 cd/A. Meanwhile, the device using TRZ-TPDICz emitter achieve a maximum EQE of 30.3 % and a maximum CE of 77.4 cd/A at green color CIE coordinates of (0.25, 0.53). This result is superior than the TRZ-pIC reference material.

Keywords: OLED, TADF, indolocarbazole, rigid donor, high efficiency





1. Introduction

Recently, thermally activated delayed fluorescent (TADF) materials for organic lightemitting diodes (OLEDs) are being actively researched.^[1-4] Nowadays, fluorescent blue and phosphorescent red and green materials are being used as primary color emitters in commercial applications. Generally, fluorescent materials utilize only a singlet exciton, thus it has a very small internal quantum efficiency (IQE) of 25 %. On the other hand, phosphorescent materials use both singlet and triplet excitons which gives IQE of 100 %.^[5,6] However, phosphorescent emitters have some disadvantages such as high cost, use of ecotoxic heavy metals and its poor device lifetime particularly in blue materials.^[7-9] Alternatively, a potential metal free organic TADF materials was demonstrated in 2012.^[10] Theoretically, TADF materials can achieve IQE of 100 % due to utilization of triplet excitons by thermally assisted reverse intersystem crossing (RISC) process.^[10-20] Generally, to achieve good TADF characteristics, reducing the gap between S_1 and T_1 energy (ΔE_{st}) is one of the main factors. The $\Delta E_{\rm st}$ is related to the degree of spatial overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). A well separated HOMO and LUMO orbitals can decrease ΔE_{st} value.^[21-24] To achieve well-separated HOMO and LUMO, the design strategy of increasing dihedral angle between the donor and acceptor is generally used.^[25-28] Thus, donors with large steric hindrance, such as acridine (Ac) or phenoxazine (PXZ) are used frequently to increase the dihedral angle.^[29-32] Apart from these donors, the well-known carbazole donor moiety is also demonstrated as a promising candidate for TADF OLED materials. However, simple carbazole is not proper due to poor donating ability and low steric hindrance. But, the carbazole derivatives such as indolocarbazole (IC) and diindolocarbazole (DI) were demonstrated as potential donor units for TADF materials as they offer higher donor strength and larger dihedral angle than simple

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carbazole.^[33-35] Particularly, indolocarbazole offers a variety of isomers depending on the positional attachment of indole nitrogen on the carbazole core as shown in Fig. 1. Also, the degree of dihedral angle and donor strength were varied depending on their isomeric structures. However, the *p*IC (para-isomeric IC) donor showed similar dihedral angle as that of carbazole. Although *p*IC showed lower dihedral angle than *o*IC (ortho-isomeric IC) and *m*IC (meta-isomeric IC) isomeric analogous, it showed similar or superior TADF performance when compared to *o*IC and *m*IC-based TADF materials.^[35,36] Thus, we envisaged that incorporation of some bulky groups on 6,12-positions of *p*IC would increase the steric hindrance between the donor and acceptor as well as two adjacent phenyl rings, which could increase the dihedral angle between donor and acceptor and the rigidity of the donor moiety. Therefore, it is expected that the dihedral angle and the PLQY would increase when compared to simple *p*IC-based TADF materials.

<**Fig.** 1>

In this work, we developed a new donor, 5,6,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TPDICz), that introduces phenyl groups at 6 and 12-positions of *p*IC framework as shown in Fig. 1. According to this design concept, we report two novel emitters, 5-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-6,11,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TDBA-TPDICz) and 5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-6,11,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TRZ-TPDICz) consisting of TDBA as rigid boron acceptor, and widely used strong triazine acceptor, respectively. Our designed material, TRZ-TPDICz showed higher dihedral angle and PLQY compared to TRZ-*p*IC reference material. By using these improved properties, the fabricated OLED device based on TRZ-TPDICz achieved a maximum EQE of 30.3 % with CIE coordinates of (0.25,

0.53). We believe that this is the first report based on TPDICz-donor and this moiety could be an excellent donor for the design of highly efficient TADF materials.

2. Experimental Section

2.1. Synthesis

All reagents for synthesizing materials were purchased from Sigma–Aldrich, TCI (SEJINCI) and used without additional purification.

2.1.1. Synthesis of N,2-Dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7sulfonamide-1,1-dioxide (DCDBTSD).^[37] A solution of sodium hydroxide (6 M, 1 mL) was added dropwise to a stirring solution of hydrochlorothiazide (0.60 g, 2 mmol) in distilled water (2 mL) during 10 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min. Then, bromine (0.16 mL, 3 mmol) was slowly added to the stirring solution of hydrochlorothiazide during 15 min at 0 °C. The insoluble brominated catalyst was removed by filtration and washed with water (10 mL) to give DCDBTSD (0.82 g, 90 %).

2.1.2. Synthesis of 6,12-Diphenyl-5,11-dihydroindolo[3,2-b]carbazole. Indole (1 g, 8.5 mmol) and benzaldehyde (0.9 g, 8.5 mmol) and N,2-dibromo-6-chloro-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide-1,1-dioxide (DCDBTSD) (0.19 g, 0.43 mmol) were stirred in acetonitrile (10 mL) at 100 °C overnight. Then, reaction mixture was diluted with ethyl acetate and extracted with water. And the moisture was removed from the organic layer using magnesium sulfate followed by concentrating the resultant. And then 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.04 g, 0.18 mmol) was added in resultant and dissolved in dimethylformamide (35 mL).^[38] After the reaction mixture was stirred at 100 °C overnight, the mixture was purified by column chromatography from methylene chloride and hexane to

give the desired product (1.0 g, 60 %) as a white solid. ¹H NMR (400 MHz, DMSO) δ 10.52 (2H, s), 7.65-7.75 (10H, m), 7.44 (2H, d, J=8 Hz), 7.25 (2H, t, J= 8 Hz), 7.06 (2H, d, J= 7.6 Hz), 6.81 (2H, t, J= 7.6 Hz)

2.1.3. Synthesis of 5,6,12-Triphenyl-5,11-dihydroindolo[3,2-b]carbazole. A mixture of 6,12-diphenyl-5,11-dihydroindolo[3,2-b]carbazole (10 g, 24 mmol), iodobenzene (5.45 g, 27 mmol), potassium carbonate (10.15 g, 73 mmol), 18-crown-6 (1.94 g, 7.34 mmol) and copper iodide (0.47 g, 2.45 mmol) in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (250 mL) was stirred at 220 °C for 48 h under nitrogen. After cooling to room temperature, the resulting mixture were added to water to obtain crystalline solid powder by filtering. The resulting product was dissolved in methylene chloride and purified by column chromatography from methylene chloride and hexane to give the desired product (6.05 g, 51 %) as a pale yellow solid. ¹H NMR (400 MHz, DMSO-d₆) δ 8.51 (1H, s), 7.70 7.76 (2H, dd, J= 11.2, 7.2 Hz), 7.03-7.26 (19H, m), 6.907 (2H, t, J= 6.8 Hz)

2.1.4. Synthesis of 5-(2,12-di-tert-butyl-5,9-dioxz-13b-boranaphtho[3,2,1-de]anthracen-7yl)-6,11,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TDBA-TPDICz). A mixture of 5,6,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (2.8 g, 5.78 mmol), 7-bromo-2,12-ditert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (2.92 g, 6.34 mmol), bis(dibenzylideneacetone)palladium(0) (0.1 g, 0.12 mmol), sodium tert-butoxide (1.11 g, 12 mmol) and tri-tert-butylphosphonium tetrafluoroborate (0.59 g, 2.02 mmol) in toluene solvent was stirred at 115 °C for 18 h under nitrogen. After cooling to room temperature, the organic layer was extracted with ethyl acetate and water, dried and concentrated. The residue was purified by column chromatography and recrystallization from methylene chloride and hexane to obtain the desired product as a pale yellow solid (2.02 g, 41 %). ¹H NMR (400 MHz, CDCl₃) δ 8.80 (2H, s), 7.81 (2H, d, J = 8.4 Hz), 7.50 (2H, d, J = 8.8 Hz), 7.36 (2H, d, J = 7.2 Hz), 7.11-7.29 (14H, m), 6.81-7.00 (7H, m), 6.74 (1H, t, J = 7.2 Hz), 6.68 (1H, d, J = 8.0 Hz), 1.53 (18H, s); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 157.2, 145.1, 144.6, 144.0, 139.1, 137.0, 136.9, 134.5, 134.1, 131.5, 130.4, 130.2, 129.7, 128.7, 128.2, 127.9, 127.1, 127.0, 126.9, 125.7, 125.5, 123.3, 123.1, 123.0, 122.7, 122.4, 121.7, 119.3, 118.9, 118.0, 113.7, 110.1, 109.8, 109.7, 34.6, 31.6 ppm; HRMS (FAB+) calcd for C₆₂H₄₉BN₂O₂ (M+H) 864.3887, found: 864.3897.

2.1.5. Synthesis of 5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)6,11,12-triphenyl-5,11dihydroindolo[3,2-b]carbazole (*TRZ-TPDICz*). This compound was obtained as an yellow solid (2.2 g, 52 %) by using a procedure similar to the synthesis of 5-(2,12-di-tert-butyl-5,9dioxz-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-6,11,12-triphenyl-5,11-dihydroindolo[3,2b]carbazole with 5,6,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (2.6 g, 5.37 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (2.29 g, 5.90 mmol) instead of 5,6,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole, 7-bromo-2,12-di-tert-butyl-5,9-dioxa-13bboranaphtho[3,2,1-de]anthracene. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (4H, d, J= 8 Hz), 8.55 (2H, d, J= 8.4 Hz), 7.62-7.68 (6H, m), 7.34 (2H, d, J= 6.4 Hz), 7.26 (2H, t, J=8.4 Hz), 7.10-7.22 (15H, m), 7.02 (1H, t, J= 8 Hz), 6.92 (1H, d, J= 8 Hz), 6.78-6.87 (3H, m), 6.68 (1H, d, J= 8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 177.7, 136.3, 132.6, 130.8, 130.7, 129.7, 129.6, 129.3, 129.0, 128.7, 128.3, 128.2, 127.1, 125.6, 125.5, 119.2 ppm; HRMS (FAB+) calcd for C₅₇H₃₇N₅ (M+H) 791.3049, found: 791.3049.

2.2. Materials Characterization

1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HATCN) was purchased from EM Index. 1,1-bis[(di-4-tolylamino) phenyl] cyclo-hexane (TAPC), and 2,2',2"-(1,3,5-

benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) were purchased from Jilin OLED Material Tech Co., Ltd. The other materials, 3,5-di(9H-carbazol-9-yl)-N,N-diphenylaniline (DCDPA), 2,8-bis(diphenylphosphine oxide) dibenzofuran (DBFPO) were synthesized by using the previously reported methods.^[39,40] For the characterization of photo-physical properties in solution, all materials were prepared in toluene solution at the concentration of 1 \times 10⁻⁵ M. The UV-vis absorption spectrum was measured by V-750 Spectrophotometer (Jasco). The solution PL spectrum and low temperature (77 K) PL spectrum were measured by FP-8500 Spectrofluorometer (Jasco). The absolute PLQY values in doped films were measured by connecting an integrating sphere to the same spectrofluorometer. These doped films were also used for transient PL measurement. Transient PL was measured when photon counts were reached until 10,000 in a nitrogen environment using Quantaurus-Tau fluorescence lifetime measurement system (C11367-03, Hamamatsu Photonics Co.). For excitation 340 nm LED light was used. The Instrument Response Function (IRF) was measured using excitation wavelength as the emission wavelength. Then, the RTPL emission peak wavelength was used for the corresponding materials. Thermal properties of newly synthesized materials were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperature (T_g) was measured by DSC graph and the decomposition temperatures (T_d) of emitters measured by TGA at 5 % weight loss.

Electrochemical analyses were performed using EC epsilon electrochemical analysis equipment. To measure the cyclic voltammetry (CV) characteristics of TADF emitters, platinum, carbon wire and Ag wire in 0.01 M AgNO₃, 0.1 M tetrabutyl ammonium perchlorate (Bu₄NClO₄), acetonitrile solution were used as counter, working and reference electrodes, respectively. For supporting electrolyte, 0.1 M tetrabutyl ammonium perchlorate

in acetonitrile solution was used. Using an internal ferrocene/ferrocenium (Fc/Fc^+) standard, the potential values were converted to the saturated calomel electrode (SCE) scale. The optical band-gap was determined from absorption onset. The LUMO level of each material was calculated from both the optical band gap and HOMO level.

2.3. Device Fabrication and Characterization

To fabricate OLEDs, Indium-Tin-Oxide (ITO) coated glass substrates (50 nm, sheet resistance of 10 ohm/square) were sequentially cleaned in ultrasonic bath with acetone, and isopropyl alcohol for 10 minutes each, and then rinsed with deionized water. Finally, substrates were dried using nitrogen followed by UV-ozone treatment for 10 minutes. All organic layers and metal cathode were deposited on the pre-cleaned ITO glass by vacuum evaporation technique under a vacuum pressure of $\sim 1 \times 10^{-7}$ torr. The deposition rate of all organic layers in was about 0.5 Å/s. Similarly, the deposition rate of LiF and Al were maintained at 0.1 Å/s, 4.0 Å/s, respectively. Finally, all devices were encapsulated using glass cover and UV curable resin inside the nitrogen filled glove box. The OLED area was 4 mm² for all the samples studied in this work. J-V and L-V characteristics of fabricated OLED devices were measured by using Keithley 2635A SMU and Konica Minolta CS-100A, respectively. EL spectra and CIE 1931 color coordinates were obtained using Konica Minolta CS-2000 spectroradiometer. All measurements were performed in ambient condition.

3. Results and Discussion

3.1. Computational properties

Molecular optimization and energy calculation on the HOMO, LUMO, S₁, T₁ levels and oscillator strength were predicted using density functional theory (DFT) and time-dependent DFT (TD-DFT) with the Schrodinger simulation program at the B3LYP/6-31G* level. The calculated data and the HOMO and LUMO orbitals localized on the optimized geometry are shown in Fig. 2. The calculated dihedral angle between donor and acceptor of TRZ-pIC was 48.5 °, whereas TRZ-TPDICz and TDBA-TPDICz showed dihedral angle of 67.5 $^\circ$ and 64.7 °, respectively. This result indicates the significance of design concept on increasing dihedral angle by attaching phenyl group. Further, we also compared the change in dihedral angle of TRZ-pIC and TRZ-TPDICz between ground state and excited state as shown in Fig. S1. The calculated dihedral angle of TRZ-pIC and TRZ-TPDICz at the excited state was 86.8 ° and 89.0°, respectively. This result indicates the change in the dihedral angle from ground state to excited state was smaller in case of TRZ-TPDICz than TRZ-pIC. Therefore, this result suggests the TRZ-TPDICz could enhance electronic transition probability results in high emission yield compared to TRZ-pIC. The calculated S₁, T₁ and ΔE st values of TDBA-TPDICz were 2.851 eV, 2.560 eV and 0.291 eV, respectively. On the other hand, the S₁, T₁ and ΔE st values of TRZ-TPDICz were 2.728 eV, 2.552 eV and 0.176 eV, respectively. As expected, the predicted ΔE st value of TRZ-TPDICz was smaller than the predicted value (0.186 eV) of TRZ-pIC reference. The calculated dipole moment of TRZ-pIC and TRZ-TPDICz was 0.20 D and 0.48 D. This result shows that TPDICz donor has more donor ability than pIC donor moiety. The HOMO and LUMO orbitals of TRZ-pIC overlapped on the phenyl linker indicates the poor HOMO and LUMO separation as shown in Fig. 2. Contrarily, the HOMO and LUMO orbitals well separated for TRZ-TPDICz and TDBA-TPDICz. Also, the calculated isovalue of 0.03 for TRZ-TPDICz and TDBA-TPDICz indicate well-separated HOMO and LUMO orbitals. This result suggests, the increased dihedral angle

Journal Pre-proof

of new materials help separation of HOMO and LUMO orbitals. The calculated HOMO values are almost similar for TDBA-TPDICz (5.443 eV) and TRZ-TPDICz (5.465 eV) because of the same donor, and these values are shallower than TRZ-*p*IC (5.549 eV). On the other hand, TDBA-TPDICz has a LUMO value of 2.676 eV and it is shallower than LUMO value of the TRZ-TPDICz of 2.855 eV due to their difference in acceptor ability. Therefore, the bandgap value of TDBA-TPDICz is 2.767 eV and TRZ-TPDICz is 2.610 eV.

<**Fig. 2**>

3.2. Synthesis and Thermal properties

The novel TPDICz donor can be synthesized using completely different synthesis method as pIC donor. The pIC donor can be synthesized from simple carbazole as almost same as other indolocarbazole like oIC and mIC, etc.^[33,35] The TPDICz donor skeleton can be synthesized by treating indole and benzaldehyde in the presence of DCDBTSD catalyst followed by treating with DDQ. After synthesizing the donor framework, partial substitution of phenyl was performed by using Ullmann coupling reaction to complete the synthesis of donor. Then, the two target materials were synthesized by a Buchwald-Hartwig coupling reaction between the donor and the corresponding acceptor units. The synthesized two emitters were purified by sublimation. The synthesis scheme of the materials is shown in Scheme 1 and the detailed synthetic method and ¹H NMR, ¹³C NMR and HRMS data are described in the experimental section. The thermal stability of the synthesized materials is important for the morphological stability and device performances. In this regard, thermal properties of the two emitters were investigated by DSC and TGA analyses. The TGA and DSC graphs are shown in Fig. S2. The thermal decomposition temperature (T_d) (5 wt% loss) of TDBA-TPDICz and TRZ-TPDICz was 428 °C, and 411 °C, respectively. The glass transition temperature (Tg) of TDBA-TPDICz and TRZ-TPDICz were observed at 211 °C,

and 181 °C, respectively. The high T_g of these materials indicate both materials possess amorphous nature and high thermal stability.

<Scheme 1>

3.3. Electrochemical and Photophysical Properties

Methods for measuring electrochemical and photophysical properties are described in the experimental section. The HOMO values of the synthesized materials in methylenechloride solution were measured by cyclic voltammetry (CV). The measured values are 5.34 eV for TDBA-TPDICz and 5.37 eV for TRZ-TPDICz (Fig. S3). Both the emitters exhibited similar HOMO value due to the presence of same donor segment. The HOMO value of TRZ-TPDICz was 0.27 eV shallower than TRZ-pIC (5.66 eV), indicates the TPDICz donor possesses stronger donating ability than *p*IC donor. This result confirms the simulation dipolemoment values. Meanwhile the band gap values were calculated from their absorption onset values measured in methylenechloride solution (Fig. S4). The calculated bandgap value of TDBA-TPDICz (2.95 eV) was larger than TRZ-TPDICz (2.89 eV) which suggests the strong donor-acceptor interaction of the later. The LUMO values were calculated using the band gap and the HOMO values and those were determined to be 2.39 eV and 2.48 eV for TDBA-TPDICz and TRZ-TPDICz, respectively. The deeper LUMO of TRZ-TPDICZ is due to stronger acceptor nature of triphenyltriazine than boron acceptor.

Further, the absorption and emission spectra of these materials were measured in toluene solution and shown in Fig. 3. The TRZ-TPDICz showed red-shifted emission than TDBA-TPDICz due to strong donor-acceptor interaction of former material. The S_1 and T_1 energies were measured from the onset point of room temperature photoluminescence (RTPL) and low temperature photoluminescence (LTPL) spectra and the data are listed in Table 1. The measured S_1 energies were 3.03 eV and 2.88 eV for TDBA-TPDICz and TRZ-TPDICz,

Journal Pre-proof

respectively. In contrary, same T_1 energy was observed for both materials. To confirm this triplet origination, we have synthesized diphenyl substituted donor unit 5,6,11,12-tetraphenyl-5,11-dihydroindolo[3,2-b]carbazole (TPDICz-Ph) and measured the LTPL spectra and shown in Fig. S5. Also, we have measured the LTPL spectra of both acceptors segments, 7-bromo-2,12-di-tert-butyl-13bH-chromeno[2,3,4-kl]xanthene (TDBA-Br) and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (TRZ-Br) and shown in Fig. S6. The LTPL spectra of two emitters and TPDICz-Ph were similar, which confirms the triplet state originated from the donor segment. The measured S_1 and T_1 values of TRZ-TPDICz were almost same compared to TRZ-pIC are quite different due to the different donor units. The emission solvatochromism of these materials were measured and shown in Fig. S8. The degrees of red-shift of emission PL peak from hexane to methylene chloride were 108 nm, 138 nm and 132 nm for TDBA-TPDICz, TRZ-TPDICz and TRZ-pIC, respectively. This result further confirms, (1) TRZ-TPDICz exhibited strong donor-acceptor interaction than TDBA-TPDICz, (2) TPDICz possesses stronger donating ability than *p*IC donor.

<**Fig. 3**>

<Table 2>

The solution and 20 wt% doped DBFPO film RTPL spectra of two novel emitters are compared and shown in Fig. S9. The doped film showed red-shifted spectra compared with solution spectra due to the polar medium of host, which stabilized the singlet energy of emitters. The stabilized energy of both emitters in doped film was 0.12 eV. Therefore, the S₁ energy of TDBA-TPDICz and TRZ-TPDICz decreased to 2.91 eV and 2.76 eV, and the reduced ΔE_{st} was 0.29 eV and 0.14 eV, respectively. Excited state lifetime of these materials were measured using time resolved photoluminescence (TRPL) spectra for 20 wt% doped

Journal Pre-proof

DBFPO film as shown in Fig. 4. Both materials exhibited both nanosecond scale excited-state prompt lifetime (τ_p) and microsecond scale excited-state delayed lifetime (τ_d) at each RTPL spectrum peak. The presence of delayed lifetime suggests the existence of TADF behavior. The calculated τ_p and τ_d of TDBA-TPDICz and TRZ-TPDICz were 26.2 ns, 7.30 μs and 30.4 ns, 8.57 µs, respectively. To confirm the TADF behavior, temperature dependent TRPL measurement was performed for these materials as 20 wt% doped DBFPO films and shown in Fig. S10. On increasing the temperature from 100K to 300K the delayed portion increases for both the materials, which confirms the involvement of TADF emission mechanism in these materials. The increase in the delayed portion is higher for TRZ-TPDICz compared to TDBA-TPDICz due to low ΔE_{st} of the former. Further, absolute photoluminescence quantum yield (PLQY) were also measured using doped films. In our previous study, TRZ-pIC obtained PLQY values of 86 %. Meanwhile the obtained PLQY values were 86 % and 96 % for TDBA-TPDICz and TRZ-TPDICz, respectively. The higher PLQY value of TRZ-TPDICz than that of TRZ-pIC reflects the computational result. By using the TRPL result and the absolute PLQY, the corresponding prompt (Φ_p) and delayed (Φ_d) components were calculated to be 68 % and 18 % for TDBA-TPDICz, 28 % and 68 % for TRZ-TPDICz, respectively. The delayed components of TDBA-TPDICz and TRZ-TPDICz showed very difference of 18 % and 68 %, because of different ΔE_{st} at the doped film of 0.29 eV and 0.14 eV, respectively.

<**Fig. 4**>

To analyze these results numerically, various rate constants were calculated by using the reported method and listed in Table 2. The radiative decay rate constant of the singlet excited state (k_r^{S}) , rate constant for intersystem crossing (ISC) from the singlet excited state to the triplet excited state (k_{ISC}) , rate constant of RISC from the triplet excited state to the singlet

excited state (k_{RISC}), and triplet non-radiative decay rate (k_{nr}^{T}) were calculated using prompt and delayed components, prompt exciton decay lifetimes and delayed exciton decay lifetimes. TDBA-TPDICz showed only two times faster k_{RISC} rate (1.15 × 10⁵ s⁻¹) compared to k_{nr}^{T} (5.91 × 10⁴ s⁻¹), which results in poor TADF performance. Whereas TRZ-TPDICz showed above 60 times higher k_{RISC} rate (3.99 × 10⁵ s⁻¹) compared to k_{nr}^{T} (0.65 × 10⁴ s⁻¹). This value was much better than the ratio of TRZ-*p*IC k_{RISC} rate (4.03 × 10⁵ s⁻¹) and k_{nr}^{T} (8.63 × 10⁴ s⁻¹). Here, TRZ-TPDICz could utilize most of the generated triplet excitons when compared to TRZ-*p*IC. Therefore, it is expected that TRZ-TPDICz would have better TADF characteristics than TRZ-*p*IC.

<Table 2>

3.4. Device Performances

To examine the TADF device performances of these new emitters, we fabricated blue and green TADF devices using DBFPO as host. The fabricated device configuration was ITO/ 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN, 7 nm)/ 1,1-bis[(di-4-tolylamino) phenyl] cyclo-hexane (TAPC, 50 nm & 60 nm)/ 3,5-di(9H-carbazol-9-yl)-N, N-diphenylaniline (DCDPA, 10 nm)/ DBFPO: 20 wt% dopant (25 nm)/ DBFPO (10 nm)/ 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, 15 & 25 nm)/ LiF (1.5 nm)/ Al (100 nm) as shown in Fig. S11. Here, HATCN was used as a hole injection layer, TAPC and TPBi were used as hole and electron transport layer, respectively. DCDPA and DBFPO were used as triplet exciton blocking (EBL) layers. Notably, there was a 10 nm thickness variation for TAPC and TPBi, due to the optimization of the optical condition.

The device performance details are shown in Fig. 5 and Table 3. The TRZ-TPDICz device showed higher luminance than TDBA-TPDICz device. The TRZ-TPDICz device exhibited maximum EQE of 30.3 % and maximum current efficiency of 77.4 cd/A with green color

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Commission Internationale de l' Éclairage (CIE) coordinate of (0.25, 0.53). This high efficiency was derived from high PLQY and high k_{RISC} . The TRZ-*p*IC reference device showed maximum EQE of 26.8 % and maximum current efficiency of 66.8 cd/A at the green color coordinates of (0.27, 0.53).³⁶ The notable thing is the maximum EQE increased near 1.13 times corresponding to the improved PLQY of TRZ-TPDICz as approximately 1.12 times compared to TRZ-*p*IC. However, the efficiency roll-off at 1,000 cd/m² was more severe in TRZ-TPDICz based device compared to TRZ-*p*IC based device. This behavior is due to longer delayed exciton lifetime of TRZ-TPDICz (8.57 µs) compared to TRZ-*p*IC (3.38 µs).

The TDBA-TPDICz device exhibited maximum EQE of 16.9 % and current efficiency of 21.4 cd/A with deep blue color coordinates of (0.14, 0.14). It showed lower efficiency than TRZ-TPDICz due to poor TADF characteristics. The EL spectra of TDBA-TPDICz showed deep blue EL spectrum peak of 462 nm which is due to weak TDBA acceptor moiety. In addition, it showed much severe roll-off characteristic than TRZ-TPDICz, which derived from the weak TADF characteristic. Though TDBA-TPDICz possessed large ΔE_{st} , it showed high efficiency. To confirm this, we calculated the expected EQE value by using the rate constants. As we previously explained, the calculated k_{RISC} of TDBA-TPDICz was 2 times faster than k_{nr}^T. Therefore, we expected that the triplet exciton up-conversion ratio would be 2 times higher than non-radiative decay, which means that 66.6 % of generated triplet excitons could be utilized for up-conversion to singlet state. Thus, the 66.6 % triplet excitons could be considered as 50 % of triplet IQE from the 75 % of triplet excitons. Hence, the total IQE of TDBA-TPDICz was calculated to be 75 % (50 % triplet + 25 % singlet excitons). Generally, without considering the molecular orientation factor, the emitter consisting of PLQY of 100 % and IQE of 100 % can emit maximum EQE of 26 %.^[30] Here, the TDBA-

TPDICz shows PLQY of 86 % and IQE of 75 %. Therefore, the theoretically calculated EQE of TDBA-TPDICz is 16.8 %, which is almost similar with experimental EQE value.

<**Fig. 5**>

<Table 3>

4. Conclusion

Two new emitters, TDBA-TPDICz and TRZ-TPDICz, based on triphenyl substituted indolocarbazole donor were designed and synthesized. The optimized geometry of these emitters showed larger dihedral angle than the TRZ-*p*IC reference material due to the presence of phenyl groups at 6, 12-positions of donor segment. The photophysical and electrochemical properties revealed that the TPDICz is relatively stronger donor than *p*IC donor. Moreover, TRZ-TPDICz showed lower ΔE_{st} and higher PLQY than TRZ-*p*IC. Therefore, the emitter TRZ-TPDICz showed superior TADF properties compared to the TRZ-*p*IC emitter. The device fabricated using TRZ-TPDICz achieved maximum EQE of 30.3 % at the green color coordinates of (0.25, 0.53) without using any optical out coupling technology. This efficiency is higher than the maximum EQE of TRZ-*p*IC (26.8 %). This is due to the lower ΔE_{st} and higher PLQY of TRZ-TPDICz originated from the large dihedral angle and high rigidity. Meanwhile, the device using TDBA-TPDICz showed a maximum EQE of 16.9 % with deep blue color coordinates of (0.14, 0.14). Based on this result we believe that our designed new donor will be applicable to design highly efficient TADF materials.

Supporting Information

The detailed synthetic procedure of TDBA-TPDICz and TRZ-TPDICz. ¹H NMR data, ¹³C NMR data, and high resolution mass spectrometry (HRMS) data. Cyclic voltammetry data.

Computational data of TPDICz-Ph, TDBA-TPDICz and TRZ-TPDICz. TGA variation graph. LTPL graph of synthesized materials. RTPL data in different polar solvents and DBFPO:20 wt% doped film. Device structure and energy diagram are available in Supporting Information.

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Fig. 1. Structure of indolocarbazole-based donors.

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Fig. 2. TD-DFT simulation results of TRZ-pIC, TDBA-TPDICz and TRZ-TPDICz calculated using B3LYP functional and 6-31G* basis set.

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Scheme 1. Synthesis scheme of materials.

35



Fig. 3. UV-vis, RTPL and LTPL spectra of (a) TDBA-TPDICz and (b) TRZ-TPDICz measured in toluene (10^{-5} M).



Fig. 4. Time-resolved PL decay curve of 20 wt% doped in DBFPO host films of the materials measured at 467 nm for TDBA-TPDICz and 511 nm for TRZ-TPDICz.

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Fig. 3. Device performances of materials. (a) Voltage vs. Luminance, (b) Luminance vs. EQE, (c) Luminance vs. Current efficiency and (d) EL spectra (inset real picture of OLED devices blue-TDBA-TPDICz and green-TRZ-TPDICz).

Table 1. Photophysical and electrochemical properties of TRZ-pIC, TDBA-TPDICz and **TRZ-TPDICz**

	λ_{abs} $^{a)}$ [$\lambda_{em}^{a)}$	S ₁ [e	T ₁ [e	$\Delta E_{\rm st}^{\ a)}$	HOMO [e	LUMO [e	Band gap ^{a)}
	nm]	[nm]	V]	V]	[eV]	V]	V]	[eV]
TRZ-pIC	403	478	2.91	2.62	0.29	5.66	2.87	2.79
TDBA-TPDICz	404	447	3.03	2.62	0.41	5.34 ^{b)}	2.39 ^{b)}	$2.95^{b)}$
TRZ-TPDICz	406	479	2.88	2.62	0.26	5.37 ^{b)}	2.48^{b}	$2.89^{b)}$
	a-5 a (b)				1			

^{a)} Toluene solution (10^{-5} M) , ^{b)} measured in methylenechloride solution.

	τ _p [ns]	τ _d [μs]	$\Phi_{_{PL}}$	Φ_{p}	$\Phi_{_{d}}$	k [10 -1 s]	k _d [10 -1 s]	k r [10 s]	k _{ISC} [10 ⁷ s ⁻¹]	$\begin{array}{c} k\\ RISC\\ 5\\ [10\\ -1\\ s\end{bmatrix}$	T k 10 s]
TRZ-pIC	13.40	3.38	0.86	0.52	0.34	7.46	2.96	3.88	3.58	4.03	8.63
TDBA- TPDICz	26.2	7.30	0.86	0.68	0.18	3.82	1.37	2.60	1.22	1.15	5.91
TRZ- TPDICz	30.4	8.57	0.96	0.28	0.68	3.29	1.17	0.91	2.38	3.99	0.65
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Table 2. Excited state lifetimes and various rate constants of TRZ-pIC, TDBA-TPDICz and TRZ-TPDICz.

30

Material	V _{on} [V]	CE _{max} ^{a)} [cd/A]	EQE ^{b)} [%] Max/@1000 nit [cd/m ²]	CIE	EL peak [nm]	FWHM ^{c)} [nm]
TRZ-pIC	3.2	66.8	26.8 / 18.6	(0.27, 0.53)	507	84
TDBA- TPDICz	3.1	21.4	16.9 / 3.5	(0.14, 0.14)	462	58
TRZ-TPDICz	3.0	77.4	30.3 / 18.4	(0.25, 0.53)	509	79

Table 3. Device performance data of TRZ-pIC, TDBA-TPDICz, and TRZ-TPDICz.

^{a)} Max current efficiency, ^{b)} External quantum efficiency, ^{c)} Full width half maximum.

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Highlights of this work:

- ✓ A new donor 5,6,12-triphenyl-5,11-dihydroindolo[3,2-b]carbazole (TPDICz) was designed and synthesized.
- ✓ TPDICz donor-based TADF material provided higher rigidity and steric hindrance compared to the reference material.
- ✓ Higher PLQY and lower ΔE_{ST} were observed for TRZ-TPDICz compared to reference TRZ-pIC.
- ✓ A maximum external quantum efficiency of 30.3% was obtained for TRZ-TPDICz as emitting dopant in TADF OLED.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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