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High-performing Bipolar Host Materials for Blue Thermally Activated Delayed Fluorescent Devices with Excellent External Quantum Efficiencies

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New bipolar host molecules composed of a carbazole, pyridoindole, and dibenzothiophene (DBT) were synthesized for blue thermally activated delayed fluorescence (TADF)-based organic light-emitting diodes (OLEDs). 2,8-Di(9*H*-carbazol-9-yl)dibenzo[*b*,*d*]thiophene, 9-(8-(9*H*-carbazol-9-yl)dibenzo[*b*,*d*]thiophen-2-yl)-9*H*-pyrido[2,3-*b*]indole, and 2,8-bis(9*H*-pyrido[2,3-*b*]indol-9-yl)dibenzo[*b*,*d*]thiophene were prepared based-on the selective reactivity at the 2,8-positions of DBT. The new symmetric and asymmetric host materials exhibited high triplet energies (2.89–2.95 eV). 4,5-Di(9*H*-carbazol-9-yl)phthalonitrile (2CzPN) was selected as an emitting dopant for achieving sky-blue emissions in TADF-OLEDs. 2CzPN-doped TADF-OLEDs whose configuration is ITO (50 nm)/HATCN (7 nm)/TAPC (75 nm)/Host:6% 2CzPN (20 nm)/TmPyPB (50 nm)/LiF (15 nm)/AI (100 nm) had low driving voltages and high external quantum efficiencies (EQEs). These results are attributed to the well-controlled bipolar character of host giving better charge balance in the emitting layer. In particular, the device containing ZDN : 6% 2CzPN had an unprecedentedly high EQE of 25.7% (at 0.074 mA/cm²).

Introduction

High quantum efficiency is an important factor in producing competitive organic light-emitting diode (OLED) devices. Until now, the focus has been on phosphorescent OLEDs (PhOLEDs), which have high quantum efficiencies based on the spin selection rule.^[1,2] In 2012, Adachi et al. described a new concept, namely thermally activated delayed fluorescence (TADF)-OLED systems, with dopant/host materials, for obtaining very high quantum efficiencies.^[3] Reverse intersystem crossing (RISC) distinguishes TADF-OLEDs from PhOLEDs or conventional fluorescent OLEDs. Effective RISC occurs when the emitting material has a small energy gap (ΔE_{ST}) between the singlet (S_1) and triplet (T_1) energy states. Facile up-conversion from the T_1 to S_1 energy state in emitting materials can enhance the external quantum efficiency (EQE) by increasing the number of excitons in the S_1 state.^[3-6] One of the keys to achieving a high EQE is that the host material for the emitting dopant must satisfy crucial requirements such as

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efficient exciton confinement. The host materials in TADF-OLEDs are similar to those in PhOLEDs, although some minor prerequisites need to be fulfilled. The host material can be a bipolar material or a mixture of two dissimilar unipolar materials.^[7,8] For a mixture of two different unipolar hosts, charge carriers can be easily injected into the emitting layer, because of the uncomplicated tuning of the energy level alignment with adjacent transport layers. However, the use of a bipolar host has the advantage of fewer interfacial contacts between adjacent layers, resulting in a lower density of trapping sites at interfaces.^[9,10] Irrespective of strong recognition of host materials, there are few host materials which were demonstrated compared to emitting dopants in TADF-OLEDs. High-performance host materials therefore need to be developed to enhance the light-emitting efficiencies of TADF-OLEDs. Among the many host materials for TADF-OLEDs, blue host molecules have been significantly less studied, because it is difficult to obtain high T_1 energies and appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for facile charge injections. In particular, achieving charge balance of the bipolar host is a barrier to obtain successful blue TADF-OLED host materials.^[11,12]

having higher S₁ and T₁ energy levels than those of the dopant,

efficient energy transfer to the dopant, low carrier injection barriers from both the carrier's transporting layers, and

In previous studies, 2,8-bis(diphenylphosphoryl)dibenzo [*b,d*]thiophene (PPT) and 1,3-di(9*H*-carbazol-9-yl)benzene (mCP) were used as host materials in 4,5-di(9*H*-carbazol-9-

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yl)phthalonitrile (2CzPN)-based sky-blue TADF-OLEDs; the corresponding devices had EQEs of around 8% and 13.6%, with the aid of auxiliary layers made of mCP and PPT to increase charge injection and transport.^[3,13] However, the performances of 2CzPN-based devices have not yet been optimized. Despite the high T₁ energies of mCP (2.90 eV) and PPT (3.02 eV), their biased carrier-transport capabilities cannot achieve the desired charge balance in the emitting layer, resulting in low EQEs in the 2CzPN devices.

Carbazole which has a rigid molecular frame, sufficiently high T₁ value, and good hole-transport property has often been used to construct host materials with desired structures for high-T₁ blue host materials.^[14] In addition, dibenzothiophene (DBT), which is thermally stable and has two reaction sites, has been used as the core unit, because it can be easily substituted with various electron-donating or withdrawing moieties such as carbazoles,^[15-19] triarylamines,^[20] cyano groups,^[21] and diphenylphosphine oxide;^[15,22] these can alter the intrinsic electronic characteristics of the bipolar host.

In addition to these moieties with electron affinities, pyrido[2,3-*b*]indole (i.e., α -carboline), which has a pyridinecontaining heteroaromatic ring, has been identified as a useful electron-accepting moiety. Recently, new carboline-based host materials consisting of carbazole and simple core materials have been shown to have highly efficient bipolar characteristics; the corresponding blue PhOLED exhibited significantly improved device efficiency.^[23–27] However, there has been no report of the use of structures containing carbazole and carboline moieties in blue TADF-OLEDs and their corresponding device efficiencies. It is therefore worth investigating how varying the number of carbazole and carboline moieties in DBT-based host materials through direct linkages affects the TADF-OLED performance.

In this study, we synthesized three different host molecules with carbazole, carboline, and DBT moieties in one molecular structure, i.e., 2,8-di(9H-carbazol-9-yl)dibenzo[b,d]thiophene (ZDZ). 9-(8-(9H-carbazol-9-yl)dibenzo[b,d]thiophen-2-yl)-9Hpyrido[2.3-b]indole (**ZDN**), and 2.8-bis(9H-pyrido[2.3-b]indol-9yl)dibenzo[b,d]thiophene (NDN). In these host molecules, we tethered carbazole and carboline units directly to the 2,8positions of the DBT unit. ZDZ bears two carbazole units, ZDN has one carbazole and one carboline unit, and NDN has two carboline units, enabling them to display different bipolar characters (Figure 1). The three host molecules have similar T₁ levels, i.e., greater than 2.89 eV. The 2CzPN-doped TADF-OLEDs had lower driving voltages (4.7-5.0 V) and significantly higher EQEs than did devices containing an mCP host. In particular, the TADF-OLED device with a ZDN host had an unprecedentedly high EQE of around 25.7 %.

Experimental

Materials

All chemicals for synthesizing the host materials were pur-chased from Aldrich, TCI, and Alfa Aesar, and were used without further

purification. 2,8-Dibromodithiophene (2),^[17] 2,8diiododibenzothiophene (4),^[28] 9*H*-pyrido[2,3-*b*]indole,^[26] and 2,8dibromodibenzothiophene 5,5-dioxide (7)^[29] were prepared using previously reported methods. Dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN), 1,1- bis[4-[*N*,*N*'-di(*p*tolyl)amino]phenyl]cyclohexane (TAPC), and 1,3,5-tri[(3pyridyl)phen-3-yl]benzene (TmPyPB) for thermally activated delayed fluorescence-organic light-emitting diode fabrication were purchased from the LUMTEC Co.



Figure 1. Molecular structures of ZDZ, ZDN, and NDN

Synthesis of 2,8-di(9H-carbazol-9-yl)dibenzo[b,d]thiophene (3, ZDZ).

2,8-Dibromo[b,d]dibenzothiophene (4 g, 11.7 mmol), 9Hcarbazole (4.4 g, 26.3 mmol), tribasic potassium phosphate (12.4 g, 58.5 mmol), copper(I) iodide (0.8 g, 4.2 mmol), and trans-1,2-diaminocyclohexane (1.3 g, 11.4 mmol) were mixed in toluene (110 mL). After purging for 30 min under Ar gas, the solution was stirred and refluxed for 12 h. The solution was cooled to room temperature and extracted with MC and water. The extracted organic layer was washed twice with water, dried with anhydrous magnesium sulfate, and evaporated under vacuum. The resulting crude product was purified by silica-gel column chromatography with MC/n-hexane (1:3) as the eluent. The obtained product was recrystallized from methanol, yielding 2.0 g (33 %) of pure product. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.32 (s, 2H), 8.18-8.14 (d, 4H), 7.75-7.72 (d, 2H), 7.44-7.28 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) : δ (ppm) 141.38, 139.47, 136.82, 135.15, 126.83, 126.32, 124.62, 123.65, 120.83, 120.66, 120.34, 109.80. Mass m/z [(M+H)⁺] Calcd. for C₃₆H₂₂N₂S: 514.15, found 515.73. Elemental analysis Calcd. for

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 $C_{36}H_{22}N_2S: \ N \ (5.44\%), \ C \ (84.02\%), \ H \ (4.31\%), \ S \ (6.23\%), \ found \ N \ (5.44\%), \ C \ (83.53\%), \ H \ (4.26\%), \ S \ (6.25\%).$



Scheme 1. Synthetic procedures for host materials: (i) bromine, methylene chloride (MC), 72 h, room temperature (rt); (ii) carbazole, K_3PO_4 , Cul, 1,2-diaminocyclohexane, toluene, 12 h, reflux; (iii) carboline, K_3PO_4 , Cul, 1,2-diaminocyclohexane, toluene, 12 h, reflux; (iv) LiAlH₄, diethyl ether, 5 h. rt.

Synthesis of 9-(8-iododibenzo[b,d]thiophen-2-yl)-9Hpyrido[2,3-b]indole (5)

2,8-Diiodo[b,d]dibenzothiophene (10 g, 22.9 mmol), 9Hpyrido[2,3-b]indole (3.8 g, 22.6 mmol), tribasic potassium phosphate (24 g, 113 mmol), copper(I) iodide (2.2 g, 11.6 mmol), and trans-1,2-diaminocyclohexane (2.5 g, 21.9 mmol) were mixed in toluene (500 mL). After purging for 30 min under Ar gas, the solution was stirred and refluxed for 12 h. The solution was cooled to room temperature and extracted with MC and water. The extracted organic layer was washed twice with water, dried with anhydrous magnesium sulfate, and evaporated under vacuum. The resulting crude product was purified by silica-gel column chromatography with MC/nhexane (1:3) as the eluent. The crude product was recrystallized from methanol, yielding 2.2 g (20 %) of pure product. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.51 (d, 1H), 8.48 (s, 1H), 8.45 (d, 1H), 8.37 (s, 1H), 8.18 (d, 1H), 8.08 (d, 1H), 7.78 (d, 2H), 7.66 (d, 1H), 7.51 (d, 1H), 7.43-7.27 (m, 3H).

Synthesis of 9-(8-(9H-carbazol-9-yl)dibenzo[b,d]thiophen-2yl)-9H-pyrido[2,3-b]indole (6, ZDN)

9-(8-Iododibenzo[*b*,*d*]thiophen-2-yl)-9*H*-pyrido[2,3-*b*]indole (2 g, 4.2 mmol), 9*H*-carbazole (0.7 g, 4.2 mmol), tribasic potassium phosphate (4.5 g, 21.2 mmol), copper(I) iodide (0.4 g, 2.1 mmol), and trans-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) were mixed in toluene (150 mL). After purging for 30 min under Ar gas, the solution was stirred and refluxed for 12 h. The solution was cooled to room temperature and extracted

with MC and water. The extracted organic layer was washed twice with water, dried with anhydrous magnesium sulfate, and evaporated under vacuum. The resulting crude product was purified by silica-gel column chromatography with MC/nhexane (1:3) as the eluent. The crude product was recrystallized from methanol, yielding 1.5 g (70 %) of pure product. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.46 (s, 1H), 8.40 (d, 2H), 8.31 (s, 1H), 8.16-8.11 (m, 5H), 7.79 (d, 1H), 8.69 (d, 1H), 7.51-7.22 (m, 10H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.40, 146.79, 141.46, 140.51, 139.78, 139.49, 137.00, 136.62, 134.94, 133.66, 128.67, 127.34, 126.99, 126.64, 126.28, 124.52, 124.38, 123.58, 121.30, 121.24, 121.09, 121.01, 120.60, 120.24, 116.62, 116.48, 110.42, 109.87, 104.99. Mass m/z [(M+H)⁺] Calcd. for C₃₆H₂₁N₃S: 515.15, found 516.15. Elemental analysis Calcd. for C₃₆H₂₁N₃S : N (8.15%), C (81.53%), H (4.11%), S (6.22%), found N (8.09%), C (81.05%), H (4.05%), S (6.36%).

Synthesis of 2,8-bis(9H-pyrido[2,3-b]indol-9-yl)dibenzo [b,d]thiophene 5,5-dioxide (8)

2,8-Dibromodibenzothiophene 5,5-dioxide (8 g, 21.4 mmol), 9*H*pyrido[2,3-*b*]indole (7.6 g, 45.2 mmol), tribasic potassium phosphate (22 g, 103.6 mmol), copper(I) iodide (2 g, 10.5 mmol), and trans-1,2-diaminocyclohexane (2.4 g, 21.0 mmol) were mixed in toluene (800 mL). After purging for 30 min under Ar gas, the solution was stirred and refluxed for 12 h. The solution was cooled to room temperature and extracted with MC and water. The extracted organic layer was washed twice with water, dried with anhydrous magnesium sulfate, and evaporated under vacuum. The

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crude product was purified by column chromatography with MC/ethyl acetate (1:1) as the eluent. The product was further purified by recrystallization from n-hexane, yielding 3.2 g (80%) of pure product. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.45 (d, 2H), 8.39 (d, 2H), 8.22 (s, 2H), 8.15-8.11 (m, 4H), 7.94 (d, 2H), 7.60 (d, 2H), 7.52 (t, 2H), 7.38 (t, 2H), 7.29 (t, 2H).

Synthesis of 2,8-bis(9H-pyrido[2,3-b]indol-9-yl)dibenzo [b,d]thiophene (9, NDN)

2,8-Bis(9H-pyrido[2,3-b]indol-9-yl)dibenzo[b,d]thiophene 5,5dioxide (2.4 g, 4.4 mmol), lithium aluminum hydride (0.8 g, 21.2 mmol), and diethyl ether (20 mL) were mixed in a 100 mL threenecked flask. The solution was stirred at room temperature for 5 h, filtered under vacuum, and extracted with MC and water. The extracted organic layer was washed twice with water and dried with anhydrous magnesium sulfate. The mixture was evaporated under vacuum. The resulting crude product was purified by column chromatography with MC/n-hexane (1:2) as the eluent. The crude product was further purified by recrystallization from methanol, yielding 0.8 g (35%) of pure product. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.46 (d, 2H), 8.42-8.39 (m, 4H), 8.14 (d, 2H), 7.78 (d, 2H), 7.51-7.44 (m, 4H), 7.36-7.22 (m, 4H). 13 C NMR (100 MHz, CDCl₃): δ (ppm) 146.84, 139.85, 136.79, 135.86, 133.54, 128.67, 127.36, 126.96, 124.37, 121.69, 121.41, 121.27, 121.12, 116.46, 114.97, 110.56, 103.51. Mass m/z [(M+H)⁺] Calcd. for C₃₆H₂₀N₄S: 516.14, found 516.85. Elemental analysis Calcd. for C₃₆H₂₀N₄S : N (10.84%), C (79.05%), H (3.90%), S (6.21%), found N (10.50%), C (78.72%), H (3.84%), S (6.03%).

Characterization

¹H and ¹³C nuclear magnetic resonance spectra were obtained using Varian Mercury 300 and 400MHz spectrometers; the solvent was CDCl₃ (Cambridge Isotope Laboratories, Inc.) Elemental analyses were performed by the Center for Organic Reactions, using an EA1112 elemental analyzer (Thermo Electron Corporation). Mass spectrometry was performed using a Bruker Daltonics, LRF-20 MALDI-TOF spectrometer. Cyclic voltammetry was used to examine the redox properties of thin films of the host materials, using a potentiostat (EA161, eDAQ). A 0.10 M tetrabutylammonium hexafluorophosphate solution in freshly dried acetonitrile was used as the electrolyte. Ag/AgCl and Pt wire (diameter 0.5 mm) electrodes were used as the reference and counter electrodes, respectively. The scan rate was 20 mV s⁻¹. Absorption spectra of the film samples were obtained using a UV-vis spectrophotometer (HP 8453, $\lambda =$ 190-1100 nm). Photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer at room temperature and a Thermo FA-357 fluorescence spectrophotometer at 77 K (solvent: 2-methyl tetrahydrofuran). The triplet energy was obtained from the highest-energy vibronic sub-band of the phosphorescence spectrum at 77 K.

Transient photoluminescence spectroscopy

The transient PL decay of 50 nm-thick 2CzPN (6 wt. %) doped host films was measured using the fluorescence lifetime spectrometer, Quantaurus-Tau from Hamamatsu Photonics Co. Prompt and delayed PL decay were achieved by irradiation of LED light source (wavelength of 340 nm and frequency of 10 MHz) and xenon lamp (wavelength of 340 nm and frequency of 100 Hz), respectively. All measurements were carried out at room temperature in dry nitrogen atmosphere. The prompt and delayed fluorescence were collected from 0 s to 50 μs and 0 to 1000 μ s, respectively. Then the exciton lifetime was calculated using single-exponential decay fitting for prompt component and triple-exponential decay fitting for delayed component. The PL quantum yields (PLQYs) of prompt and delayed components were calculated individually using UV absorbance, prompt and delayed PL integral intensities of each film at the wavelength of 340 nm.



Figure 2. Molecular structures and HOMO/LUMO distributions of ZDZ, ZDN, and NDN, obtained using Gaussian09W with the B3LYP/6-31G* basis set.



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Figure 4. (a) UV-vis absorption, solid-state PL, and low-temperature PL (LTPL) spectra of ZDZ, ZDN, and NDN. Transient PL decay curves (b), prompt components of PL spectra (c), and delayed component of PL spectra (d) of mCP, ZDZ, ZDN, and NDN films doped with 2CzPN (6 wt%).

able 1. Photophysical and electrochemical properties of mCP, ZDZ, ZDN, and NDN									
Material	Absorption ^a [nm]	PL ^{<i>a</i>} [nm]	λ _{cutoff} ^α [nm]	Eg ^{opt b} [eV]	<i>E</i> τ ^c [eV]	E _{ox} ^d [V]	HOMO ^d [eV]	LUMO ^e [eV]	
mCP	297, 343	379	353	3.51	2.90	0.88	-5.68	-2.17	
ZDZ	294, 327, 341	378	352	3.52	2.94	0.91	-5.71	-2.19	
ZDN	294, 341	378	359	3.45	2.92	0.92	-5.72	-2.27	
NDN	298, 335	380	362	3.43	2.89	1.02	-5.82	-2.39	

^a The values were obtained from solution spectra in chloroform. ^b The values were calculated from the absorption edges (λ_{cut-} _{off}), $E_g^{opt} = 1240/\lambda_{cut-off}$.^c The triplet energies were measured at 77 K in 2-methyltetrahydrofuran solution. ^d E_{ox} value and HOMO energy were measured by CV.^e LUMO energy was calculated from the difference between the HOMO and E_g^{opt}.

Device fabrication and measurements

The devices were fabricated using a clean glass substrate coated with a 150 nm thick indium tin oxide (ITO) layer, with a sheet resistance of 10 Ω/cm^2 , as the anode. An active pattern size of $2 \times 2 \text{ mm}^2$ was formed using photolithography and wet etching processes. The structure of the blue thermally activated delayed fluorescence OLED device was ITO (50 nm)/HATCN (7 nm)/TAPC (75 nm)/2CzPN 6 wt% doped host material (20 nm)/TmPyPB (50 nm)/LiF (1.5 nm)/Al (100 nm). The current density-voltage-luminance (J-V-L) data for the

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blue TADF-OLEDs were obtained using a Keithley SMU 238 instrument and a Minolta CS-100A colorimeter. The electroluminescence (EL) spectra were obtained using a Minolta CS-2000 spectroradiometer. All EQE values were measured with an integrating sphere instrument (Photal Labsphere).

Results and discussion

Synthesis and theoretical calculation

The three host materials were easily synthesized by Ullmann coupling reaction as shown in Scheme 1. However, when anchoring carboline units into dibromodibenzothiophene (2) or diiododibenzothiophene (4), the reaction yield was found much lower than that of ZDZ. In order to improve the reaction yield for NDN, the compound 4 was oxidized to generate stronger electron withdrawing compound, 2,8dibromodibenzothiophene 5,5-dioxide (**7**). When using compound 7, the reaction yield for NDN was much improved. The synthesized host materials were purified using silica-gel column chromatography as wet process and vacuum sublimation as dry process in succession. ZDZ contains two carbazole units, at the 2- and 8-positions of the DBT core, and NDN has two carboline units at the same DBT positions. ZDN is asymmetric and has one carbazole and one carboline unit. Density functional theory calculations were used to optimize the molecular structures and HOMO and LUMO distributions, using the B3LYP/6-31G* basis set. The HOMO and LUMO states of the three host materials are shown in Figure 2. The electron densities in the HOMOs of ZDZ and NDN are delocalized across the entire molecules, whereas the electron density in ZDN is localized mainly on the carbazole and a small part of the DBT moiety. The electrons in the LUMO states of the three host molecules are concentrated on the DBT unit, because of the lower-lying LUMO level resulting from the electron affinity of the sulfur atom.^[15] These results show that ZDN can provide hole and electron pathways and shows the characteristics of bipolar host materials more predominantly.

Electrochemical and photophysical properties

The molecular energy levels of the host materials are crucial for achieving efficient charge injection and energy transfer. The first oxidation potentials of **ZDZ**, **ZDN**, and **NDN**, determined using cyclic voltammetry, were 0.91, 0.92, and 1.02 V, respectively (**Figure 3** and **Table 1**). Accordingly, the HOMO levels of **ZDZ** and **ZDN** were calculated to be -5.71 and -5.72 eV, respectively; these are higher by 0.10 eV than that of **NDN** (-5.82 eV). The LUMO levels of **ZDZ** and **ZDN** were -2.19 and -2.27 eV, respectively, which is higher lying than that of **NDN** (-2.39 eV). These results show that as the number of carboline units in the host material increases, lower-lying HOMO and LUMO levels are observed.

The photophysical properties of the three host materials were investigated using UV-vis absorption and PL spectroscopies. **Figure 4a** displays the UV-vis absorption, PL, and LTPL spectra of the three host materials. All the host materials had strong absorption peaks at around 290 nm, assigned to π - π * transitions, and weak absorption peaks in the range 330–350 nm, which originate from n- π * transitions. The optical bandgap energies (E_g^{opt}), determined from the absorption edges ($\lambda_{cut-off}$), were 3.51, 3.45, and 3.43 eV for **ZDZ**, **ZDN**, and **NDN**, respectively. The maximum PL emission wavelengths of thin films of the three hosts were observed at around 380 nm and the spectra overlapped well with the absorption spectrum of 2CzPN, as shown **Figure S1**. The highest energy PL peaks at 77 K were observed at 420, 427, and 429 nm for **ZDZ**, **ZDN**, and **NDN**, respectively. High T₁ levels, i.e., 2.95, 2.90, and 2.89 eV, were therefore calculated for **ZDZ**, **ZDN**, and **NDN**, respectively; these are high enough to confine the triplet (2.5 eV) energy of 2CzPN.^[30]

To evaluate the relationship between the chemical structure and TADF characteristics of the host materials, transient PL spectra of thin films of the 2CzPN-doped hosts were acquired using a xenon light source. Figure 4b and Figure 4c-d show the transient PL decay curves and normalized emission spectra of 50 nm thick 2CzPN (6 wt.%)-doped host films at room temperature. Their detailed data are displayed in Table 2. As shown in Figure 4b, a delayed component was clearly observed for all host materials about 40 µs after initiation of the prompt component. The delayed exciton lifetime (τ_d) of 2CzPN was determined to be 246.15 µs for the mCP host. This value is in good agreement with the previously reported τ_d (273 µs) of the mCP:2CzPN system.^[13] Delayed exciton lifetimes of 228.85, 208.82, and 135.41 μs were observed for the ZDZ, ZDN, and NDN host materials, respectively. The exciton lifetimes of 2CzPN changed significantly based on the host materials. 2CzPN had a shorter exciton lifetime in the DBT-based host materials than in the mCP host. Notably, the exciton lifetime of 2CzPN became even shorter as the number of carboline moieties in the host increased. As shown in Figure 4d, there was a slight red-shift of the PL peak wavelength of 2CzPN from 482 nm in mCP to 501 nm in the NDN host. The emission of all the newly developed host materials was slightly red-shifted relative to that of mCP. It is postulated that a weak interaction is active in the solid state film when the TADF dopant material is surrounded by polar moieties that can stabilize the singlet excited state, akin to solvatochromic behavior.^[31] Higher stabilization by the host material results in a larger red-shift of the emission. Transient PL spectra were also acquired using a LED light source for precise determination of the prompt exciton lifetimes. The prompt exciton lifetimes (au_p) of the host molecules were determined to be 14.63 ns (mCP), 26.37 ns (ZDZ), 15.76 ns (ZDN), and 19.54 ns (NDN). The measured prompt lifetime of the 2CzPNdoped mCP film was also consistent with the reported value of 16 ns.^[13] Figures 4c and 4d show the normalized prompt and delayed PL spectra of the four 2CzPN-doped host films.

The profiles of the prompt PL spectra are almost identical to that of the delayed PL spectra. The prompt PL maximum wavelength was also red-shifted from 485 nm in mCP to 498 nm in the NDN host. The relative PLQY of these films was derived by comparison with the reported PLQY of the 2CzPNdoped mCP films from Ref. 10; the total PLQY was 89% when

the prompt	and	delayed	components	were	51%	and	38%,	
respectively.								
Table 2, Pho	otoph	nysical pro	operties of ho	st mat	erials	dope	d with 2C	7PN

Host	τ _p [ns]	τ _d [μs]	$arPsi_{ extsf{F}}$	$arPsi_{ extsf{TADF}}$	k_{p} [s ⁻¹]	k_{d} [s ⁻¹]	k_{r}^{S} [s ⁻¹]	k_{ISC} [s ⁻¹]	k_{RISC} [s ⁻¹]	k_{nr}^{T} [s ⁻¹]
mCP	14.63	246.15	0.510 ^[10]	0.380 ^[10]	6.83×10^{7}	4.06×10^{3}	3.49 × 10 ⁷	3.35×10^{7}	6.18×10^{3}	9.12×10^{2}
ZDZ	26.37	228.85	0.440	0.401	3.79×10^{7}	4.37×10^{3}	1.67×10^{7}	2.12×10^{7}	7.11×10^{3}	1.24×10^{3}
ZDN	15.76	208.82	0.495	0.487	6.35×10^{7}	4.79×10^{3}	3.14×10^{7}	3.20×10^{7}	9.33×10^{3}	1.71×10^{2}
NDN	19.54	135.41	0.434	0.445	5.12×10^{7}	7.38×10^{3}	2.22×10^{7}	2.90×10^{7}	1.34×10^{4}	1.58×10^{3}

The total relative PLQY was determined to be 84.1% for the ZDZ host film, 98.2% for the ZDN host film, and 87.9% for the NDN host film. The respective prompt and delayed components of the PLQY of 2CzPN were 40.1% and 44.0%, 48.7% k_{Tr}^{T} values for ZDZ and NDN were estimated to be about 1.4 and 49.5%, and 44.5% and 43.4% for ZDZ, ZDN, and NDN, respectively. The DBT-based host films showed higher delayed PLQY compared to mCP, which was particularly pronounced for ZDN, while the prompt PLQY of the DBT-based host films was lower than that of the mCP host film. This indicates that the DBT-based host enhanced the TADF characteristics of 2CzPN.

To further understand the mechanism underlying the TADF of the host materials, the kinetic parameters of the 2CzPNdoped films were estimated based on the experimental results (Table 2). The radiative decay rate constant of the singlet excited state (k_r^S) , the rate constant for intersystem crossing (ISC) from the singlet excited state to the triplet excited state (k_{ISC}) , the rate constant for reverse intersystem crossing (RISC) from the triplet excited state to the singlet excited sate (k_{RISC}) , and the non-radiative (nr) decay rate constant for the triplet excited state (k_{nr}^T) were calculated using the following equations based on the assumption that the non-radiative decay rate constant of the singlet excited state (k_{nr}^S) is zero at room temperature.^[13]

$$k_r^S = k_p \phi_F \tag{1}$$
$$k_{ISC} = k_n (1 - \phi_F) \tag{2}$$

$$k_{RISC} = \frac{k_p k_d}{k_{ISC}} \frac{\phi_{TADF}}{\phi_F}$$
(3)
$$k_{nr}^T = k_d - k_{RSIC} \phi_F$$
(4)

$$k_{nr}^T = k_d - k_{RSIC}\phi_F$$

Here, k_p and k_d denote the prompt and delayed fluorescence decay rate constant (where $k_p = 1/\tau_p$ and $k_d = 1/\tau_d$), ϕ_F and ϕ_{TADF} are the prompt and delayed fluorescence quantum efficiencies, respectively. The value of k_{RISC} for the DBT-based host materials was estimated to be 1.2 (ZDZ), 1.5 (ZDN), and 2.2 (NDN) times higher than that of mCP. Interestingly, the k_{RISC} increased with an increase in the number of carboline moieties in the host. The singlet-triplet

exchange energy (ΔE_{ST}) apparently decreased with stabilization of the singlet excited state. This result is consistent with the previous PL spectral shifts. The respective and 1.7 times larger than that of mCP, resulting in the poor total PLQYs of ZDZ and NDN. On the other hand, the ZDN host material shows more balanced polarity and it could properly stabilize the singlet state of 2CzPN. Similarly, it also increases the k_{RISC} by reducing $\varDelta E_{\rm ST}$, and displays small increase in k_d . These increased rates naturally decrease the k_{nr}^T . The decreased k_{nr}^T of ZDN is about one-fifth than that of the mCP host. However, too much stabilization by NDN host could increase k_{nr}^{T} and reduce PLQY with interaction increase of vibration bands.^[31,32] Hence, an almost 100% PLQY of the 2CzPN TADF dopant was estimated in the ZDN host due to the high k_{RISC} and low k_{nr}^T (Table S1).

TADF-OLED performance

In order to investigate the performance of the new materials as a host, blue TADF-OLEDs were fabricated using 2CzPN as a blue dopant. A mCP-based device was also fabricated and used as a reference. Herein, we employed HATCN as a hole injection layer. Similarly, TAPC and TmPyPB were used as respective hole and electron transporting layers due to their high T₁ energy. The high T₁ of these transport layers can easily prevent quenching of the exciton triplet of the dopant (2CzPN) at the interface of HTL-EML and EML-ETL.

A blue TADF-OLED device was fabricated with the ITO (50 nm)/HATCN (7 nm)/TAPC (75 nm)/2CzPN 6 wt%:host (ZDZ, ZDN and NDN) (20 nm)/TmPyPB (50 nm)/LiF (1.5 nm)/AI (100 nm) structure. The J-V-L characteristics of the fabricated blue electroluminescent devices are shown in Figure 5a. The operating voltages at 1000 cd m⁻² were determined to be 5.0, 4.7, and 4.8 V, respectively, for the ZDZ-, ZDN-, and NDN-based OLED devices; these values are much lower than those of the control device (6.2 V). Figure 5b shows the external quantum efficiency (EQE) curves of the OLED devices. EQEs of 4.0%, 4.9%, 6.0%, and 4.7% were achieved at a brightness of around 1000 cd m⁻² for the mCP, ZDZ, ZDN, and NDN devices, respectively. As expected from previous PL studies, the ZDN device exhibited the best TADF device performance among the four host-based devices. The maximum EQE of 25.7% was observed at the current density of 0.08 mA cm⁻² for the ZDN

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device. The NDN device also had a quite high EQE of 23.9% at the current density of 0.05 mA cm $^{-2}$.



Figure 5. J–V–L curves (a), EQE–L curves (b), CE–L curves (c), and electroluminescence (EL) spectra (d) of blue TADF-OLEDs fabricated using three new hosts and 2CzPN dopants.

Table 3. El	lectroluminesc	ent properties	s of the fabrica	ated TADF-OL	EDs with new	host materia	ls	
Host	Voltage ^a [V]	CE ^{<i>a</i>} [cd A ⁻¹]	CE ^b [cd A ⁻¹]	EQE ^a [%]	EQE ^b [%]	EQE ^c [%]	luminance ^b [cd m ⁻²]	CIE ^{<i>a</i>} [x, y]
mCP	6.2	8.53	23.87	4.0	14.0	19.4	4257	0.17, 0.32
ZDZ	5.0	10.72	31.83	4.9	18.5	17.8	3231	0.17, 0.34
ZDN	4.7	14.29	53.05	6.0	25.7	24.0	6366	0.19, 0.39
NDN	4.8	11.82	47.74	4.7	23.9	19.5	10711	0.20, 0.42

Measured at 1000 cd m⁻², maximum values, theoretically calculated.

The extremely high quantum efficiencies of the ZDN and NDN devices at the very low current density are attributed to the larger k_{RISC} of the 2CzPN dopant in both host materials and proper charge balance in the emissive layer. On the other hand, the overall efficiency of the ZDN device was much higher than that of the NDN device because the k_{nr}^T of the NDN host is 9.2 times larger than that of the ZDN host, which causes an efficiency drop in the higher current density region for the NDN device. The theoretical EQEs of the OLEDs with the new TADF host materials were evaluated using a previously

reported equation.^[32] The photon out-coupling efficiency and charge balance factor were considered as 25% and 100%, respectively. The theoretical EQE values calculated from the PL data are summarized in **Table 3**. The calculated EQE values of all three host-based devices show quite good agreement with the measured performance. In particular, the theoretical and measured EQE values for the ZDN device agree within 0.7% error. The EQE value of the NDN device (4.7%) was even lower than that of the ZDZ device (4.9%) at a brightness of 1000 cd m⁻², despite the much better *J-V* characteristics of the NDN

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device. The maximum EQEs of the mCP and ZDZ devices were 14.0% and 18.5% at the respective current densities of 0.1 mA cm⁻² and 0.05 mA cm⁻². The performance parameters of the respective host devices are compared in **Table 3**. The maximum luminance of the DBT-based host devices increased with increasing numbers of carboline moieties due to the electrically stable characteristics of carboline compared to the carbazole moiety.^[33] A maximum luminance of over 10 000 cd m⁻² was achieved with the NDN device. **Figure 5d** shows the normalized EL spectra of the four fabricated devices at a brightness of 1000 cd m⁻².

The EL spectra of the OLEDs of the DBT host devices were also slightly red-shifted relative to that of the mCP device, similar to the trend observed for the PL. The wavelengths of maximum emission were 485, 489, 494, and 494 nm for the mCP, ZDZ, ZDN, and NDN host materials. The singlet excited state of the 2CzPN TADF dopant could be stabilized by the host molecules that contained DBT and carboline moieties. As a result, the TADF characteristics of 2CzPN were enhanced due to the increased k_{RISC} and suppression of the k_{nr}^{T} , especially in the ZDN host molecule.

Conclusions

New host materials containing carbazole, carboline, and DBT moieties successfully boosted the EQEs of blue TADF-OLEDs. The structures of the three host materials were precisely varied to accomplish different partial positive and negative charge affinities in the solid state. All host materials had sufficiently high triplet energies, suitable HOMO and LUMO levels, and balanced charge densities in the emitting layers of blue TADF-OLEDs. Almost 100% PL quantum yield was achieved with the ZDN molecule due to the high k_{RISC} and low non-radiative decay. Among the four devices, the devices bearing ZDN displayed significantly higher EQEs, i.e., 25.7% at 0.077 A cm $^{\text{-2}}$ and 5.5% at 10 mA cm $^{\text{-2}}.$ The device efficiency could be further improved simply by tuning the electronic characteristics with the carboline tethered to the DBT core; therefore, carbazole and carboline building blocks anchored to the DBT unit as a host is a promising molecular design for further development of efficient blue TADF-OLEDs.

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Graphical Abstract

The newly synthesized host materials exhibited high triplet energies in the range of 2.89–2.95 eV, which is useful in thermally activated delayed fluorescence (TADF)-based OLED. They show stabilization of the singlet state which results in an improved reverse intersystem crossing rate constant owing to the small singlet-triplet energy gap with respect to the polarity of the host molecules. The 2CzPN-based blue TADF devices with a ZDN host had an unprecedentedly high external quantum efficiency of 25.7%.

