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Two Channel Emission Controlled by Conjugation Valve for Color Switching of Thermally Activated Delayed Fluorescence Emission

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Abstract

Development of two channel emission featured deep blue thermally activated delayed fluorescent (TADF) emitters is highly challenging due to their unavoidable extended conjugated structures. Herein, we propose a simple and effective interconnection position engineering strategy to control their emission color in deep blue region through a conjugation valve with uncompromised external quantum efficiency (EQE). Two novel TADF emitters named 2,3',4,5'-tetra(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-3,4'-dicarbonitrile (**34CzBN**) and 3,3',5,5'-tetra(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-4,4'-dicarbonitrile (**44CzBN**) were developed to utilize two channel emission path by directly connecting two identical TADF units to have different degree of conjugation. The non-conjugative mode of connection in **34CzBN** resulted in significant blue-shift in absorption and emission compared to its isomer **44CzBN**. The two channel emission process provided four times higher EQE than the single channel emission process. The **34CzBN** based TADF device demonstrated deep blue emission with a color coordinate of (0.14, 0.14) due to closed conjugation channel and EQE of 15.2%. Whereas, the

44CzBN device showed green emission with a color coordinate of (0.20, 0.44) due to opened conjugation channel and EQE of 13.8%. Additionally, the emission spectrum of the **34CzBN** based device became narrow (full width at half-maximum \sim 63 nm) due to restricted molecular motion by interlocked carbazole donor at central core.

Key words : two channel emission, blue, TADF, efficiency

Introduction

During the past three decades, organic light emitting diodes (OLEDs) received immense interest from both academia and industry due to their distinct advantages over the inorganic light-emitting diodes such as light weight, improved picture quality and contrast, flexibility, fast response times and low power consumption.^{1,2} In the OLEDs, the recombination of charge carriers produces 25% singlet and 75% triplet excitons in accordance with the spin statistics.²⁷ According to spin selection rules, fluorescent emitters can utilize only one quarter of excitons for light emission, which limits their internal quantum efficiency to 25%.¹⁻³ Meanwhile, phosphorescent emitters can harness both the singlet and triplet excitons for light emission to achieve 100% internal quantum efficiency.³ However, the use of expensive rare metals and short lifetime of precious metal-based deep-blue phosphorescent emitters for OLEDs are challenging issues.² To overcome these issues, *metal-free* thermally activated delayed fluorescence (TADF) based organic emitters attracted significant attention due to their 100% theoretical exciton utilization for light emission by harvesting non-emissive triplet excitons through favorable reverse inter system crossing (RISC) from triplet excited state (T_1) to singlet excited state (S₁).^{2,4} In principle, small singlet-triplet energy splitting (ΔE_{ST}) is essential to ensure efficient RISC.^{2,4} It has been demonstrated that the donor-acceptor (D-A) type molecular

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design with twisted geometry is highly desirable to reduce the ΔE_{ST} through well separation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).² In addition to the high RISC, high photoluminescence quantum yield (PLQY) is also an important parameter of the TADF emitter and several strategies have been successful to reach the high PLQY value in the TADF emitters. For instance, multiple donor based molecular design, HOMO dispersing molecular design, and multiple TADF units based molecular design improved the PLQY of the TADF emitters.^{5,6}

Among all the colors of TADF emitters, efficient deep blue TADF emitters with CIEy ≤ 0.15 rarely reported in the literature, because as mentioned above the basic design of TADF emitter adopts D-A type molecular structure, which always leads to broad (FWHM ~ 70-100 nm) and red-shifted emissions.⁷⁻²⁸ Moreover, simultaneous achievement of small ΔE_{ST} , deep blue emission and high PLQY is highly challenging task.7-28 Therefore, the development of efficient deep blue TADF emitters became one of the grand challenges to the researchers. It has been demonstrated that the utilization of two channel emission is an effective strategy to boost the EQE of TADF emitters compared to single channel emission.⁶ However, this approach was unsuccessful for the development of deep blue emitters (CIEy ≤ 0.15) because of their increased degree of conjugation and strong charge transfer interactions.⁶ Therefore, the new molecular design for the development of two channel emission featured efficient deep blue TADF emitters is desirable. Recently, Adachi et al. reported high triplet energy deep blue emitter (DCzBN1) with good color purity (CIEy ~ 0.05), but the emitter demonstrated poor external quantum efficiency (EQE) of 2.5% due to the large $\Delta E_{\rm ST}$ (0.31 eV) and inefficient RISC.¹⁹ Here, we intended to utilize this backbone structure to develop two channel emission based TADF emitters. We expect that the connection of two identical high triplet energy deep blue TADF units can open two channel emission and the control of the degree of conjugation can manage the emission color. The coupling of two emitting cores can improve the PLQY and

can effectively utilize the two channel emission process for boosting the overall EQE.

In this contribution, we developed two novel TADF emitters named 2,3',4,5'-tetra(9Hcarbazol-9-yl)-[1,1'-biphenyl]-3,4'-dicarbonitrile (34CzBN) and 3,3',5,5'-tetra(9H-carbazol-9yl)-[1,1'-biphenyl]-4,4'-dicarbonitrile (44CzBN) by connecting two identical emitting units through different positions. The interconnect position played a role of a conjugation valve by opening and closing the conjugation channel through steric hindrance, which switched the emission color between green and deep blue colors. The non-conjugative mode of linkage between two emitting units of 34CzBN produced severe steric hindrance at central core with large distortion, which interrupted the effective degree of conjugation and resulted in significant blue-shift of absorption and emission profiles compared to its structural isomer 44CzBN. Moreover, the two channel emission via the two TADF units of 34CzBN and 44CzBN improved the EQE of the devices by four times compared with the single TADF unit **CzBN**. A high EQE of 15.8% with a deep blue color coordinate of (0.14, 0.14) and an EQE of 13.8% with a green color coordinate of (0.20, 0.44) were demonstrated for the **34CzBN** and 44CzBN based devices, respectively. We believe that our molecular design would provide fundamental insights to design efficient two channel emission featured deep blue TADF emitters.

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Scheme 1. Synthetic protocol of the compounds

Results and Discussions

Molecular design and synthesis



Fig. 1 Design concept of two channel emission featuring TADF materials.

Molecular design concept of this work is that the connection of two identical high triplet energy deep blue emitting cores in a non-conjugative mode through a phenyl linker with severe steric hindrance at central core can disrupt the planarity and hinder the effective conjugation thought the molecule (Figure 1). As a result, the emission color can fall in deep blue region with small ΔE_{ST} and high PLQY. In addition, two channel emission process can be effectively utilized to promote the overall EQE of deep blue TADF emitters. Whereas, the connection of two TADF units in a conjugative mode without steric hindrance can extend the conjugation and the emission color can be shifted to long wavelength while maintaining the small ΔE_{ST} , high PLQY, and high EQE due to two channel emission process. Therefore, high efficiency

TADF emitters with different emission colors can be developed using the same building blocks. The interconnect position can play a role of conjugation valve for opening and closing the conjugation channel and managing the emission color.

Two novel TADF emitters, 34CzBN and 44CzBN, with different degree of conjugation were developed to rationalize the design concept. The synthetic procedure to synthesize the target materials is illustrated in Scheme 1. The key aryl fluoride intermediates such as 3 and 6 were prepared in two step synthetic protocol starting from the boronate ester formation of 1 and 4 using palladium-catalyzed reaction conditions.²⁹ Subsequently, the intermediates 2 and 5 were treated with 4 under palladium-catalyzed Suzuki-Miyaura cross-coupling reaction conditions to yield aryl fluoride intermediates **3** and **6** in good yield, respectively.³⁰ Finally, the fluoride intermediates 3 and 6 were allowed to react with 4.0 eq. of 9H-carbazole using cesium carbonate mediated nucleophilic substitution reaction to obtain the desired 34CzBN and 44CzBN TADF emitters in reasonable yields. The compound 2,6-di(9H-carbazol-9yl)benzonitrile (CzBN) were synthesized as per the given procedure in the literature.¹⁹ We also tried to synthesize the additional isomer in the series by connecting two CzBN cores via 3,3'positions of phenyl linker using various synthetic methods, but the synthesis was unsuccessful due to the large steric hindrance. The chemical structures of the 34CzBN and 44CzBN compounds were confirmed by the spectroscopic analysis such as nuclear magnetic resonance spectroscopy (¹H NMR and ¹³C NMR), elemental analysis and mass spectroscopy. The materials were purified by the vacuum train sublimation procedure before application in the OLED devices.

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Fig. 2 Optimized geometries and FMO distributions of the compounds estimated using DFT computations

Theriotical Caleculations

To understand the effect of interconnection position of the two channel emission featured TADF materials on their frontier molecular orbital distributions (HOMO and LUMO) and ΔE_{ST} , density functional theory (DFT) computations were implemented on the TADF compounds employing M062X/6-31G(D) basis set on Gaussian 16 program. The optimized geometries and their frontier molecular orbital (FMO) distributions of the compounds are shown in Figure 2. The dihedral angle between directly connected two emitting cores is dependent on the linking

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position. The dihedral angles (α) between the two phenyl units of biphenyl core of **34CzBN** and 44CzBN are 55 and 36°, respectively. The two phenyl units of 34CzBN is largely distorted due to the large steric hindrance by the interlocked carbazole donor at ortho-position of the phenyl linker with a large dihedral angle (β) of 71°. As a result, the effective π -conjugation in the **34CzBN** emitter can be interrupted. Whereas, the small dihedral angle between two phenyl units of 44CzBN extends the π -conjugation. The connection of the two TADF CzBN units via C4 & C4 position opens the π -conjugation channel, while that via C3 & C4 position closes the π -conjugation channel. The dihedral angle (γ) between the carbazole donor and phenyl linker of **34CzBN** and **44CzBN** is analogues to that of the **CzBN**. The interconnection position and dihedral angle also affected the HOMO and LUMO distributions. In the case of 44CzBN, the HOMO is uniformly dispersed over the all four carbazole units because of the existence of extensive conjugation between all the carbazole donors through a small dihedral angle (α) between two emitting cores. Whereas, in the case of **34CzBN**, the HOMO was non-uniformly distributed due to the electronically separated carbazole donor units by large steric hindrance at the biphenyl unit. In the two compounds, the LUMO was mainly localized on the biphenyl linker and cyano acceptor. Although the FMO distribution is different in these compounds, the well separated HOMO and LUMO orbitals with partial overlap on the biphenyl unit fulfilled the requirement of TADF emitters. The calculated singlet (S_1) /triplet energies $(T_1)/\Delta E_{ST}$ of the compounds were 3.84/3.58/0.26 eV for CzBN, 3.58/3.27/0.28 eV for 34CzBN and 3.41/3.18/0.23 eV for 44CzBN. The closed π -conjugation channel of the 34CzBN emitter by large twisting angles is responsible for the high singlet and triplet energies compared to 44CzBN with opened π -conjugation channel.



Fig. 3 Absorption spectra of the compounds recorded in THF solution.

Photophysical Properties

To understand the correlation between the molecular structure and absorption and emission properties of the materials, photophysical properties were investigated by ultraviolet-visible (UV-vis) absorption and fluorescence spectrometer. The absorption spectra of the compounds collected in tetrahydrofuran (THF) solution are shown in Figure 3, and the detailed data are listed in Table 1. The compounds showed multiple absorption bands in the range of 270-450 nm. The short wavelength bands between 250 and 340 nm are attributed to the localized π - π * electronic transitions of the aromatic segments. The long wavelength absorption band above 350 nm stems from the intramolecular charge transfer (ICT) from the carbazole donor to cyano acceptor. In the UV-vis absorption data, the molar extinction coefficient of the **34CzBN** and **44CzBN** emitters increased significantly compared to that of the **CzBN** because of intensified

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light absorption by the two light absorbing TADF units. In particular, the **44CzBN** emitter showed even higher molar extinction coefficient at short wavelength region (< 300 nm) than **34CzBN** because of extended conjugation throughout the molecular structure with small twisting angle (α). The comparison of the absorption profiles of the compounds revealed that the absorption edge depends on the number of chromophores and their interconnect position. The ICT band was red-shifted in the **34CzBN** and **44CzBN** emitter relative to that of **CzBN** due to the increased charge transfer interactions between carbazole donor and cyano acceptor and extended π -conjugation. Indeed, the **34CzBN** showed blue-shifted absorption compared to **44CzBN** due to the interrupted conjugation between the two emitting units.

The photoluminescence (PL) spectra of the compounds recorded using 10 wt% emitter doped bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) films are shown in Figure 4. The trend of emission profiles of the compounds is in good agreement with the absorption profile, confirming the effect of interconnect position and dihedral angle. The increasing order of emission wavelengths of the compounds are CzBN (403 nm) < 34CzBN (453 nm) < 44CzBN (490 nm). The 44CzBN and 34CzBN displayed 50 and 87 nm red-shifted emission compared to CzBN. As expected, the large dihedral angle of 34CzBN allowed the deep-blue emission by minimizing the degree of conjugation, while the small dihedral angle of 44CzBN leads to the green emission.

Furthermore, the nature of the excited state of the compounds was investigated by solvatochromic study. The emission profiles of the compounds were progressively red-shifted by increasing the solvent polarity from non-polar cyclohexane (CH) to polar dichloromethane (MC) (Figure 5).³¹ Generally, the red-shifted broad emission in polar solvents indicates charge transfer (CT) excited state of the compounds.³¹ The **34CzBN** emitter displayed weak CT in the excited state as evident from the small bathochromic-shift ($\Delta\lambda_{(CH-ACN)} \sim 39$ nm) compared to

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its isomer 44CzBN ($\Delta\lambda_{(CH-ACN)} \sim 75$ nm) and even the CzBN ($\Delta\lambda_{(CH-ACN)} \sim 45$ nm). This is attributed to the limited conjugation between the two emitting units with large dihedral angle in 34CzBN, which restricted the strong CT in the excited state.³¹ The phosphorescence spectra of the compounds recorded in frozen THF at 77 k exhibited the similar tendency to the fluorescence spectra. The S₁ and T₁ energies of the CzBN, 34CzBN and 44CzBN were estimated from their onset wavelengths of fluorescence and phosphoresce spectra and were 3.40/3.10 eV, 3.18/2.96 eV and 2.95/2.80 eV, respectively. As expected, the T₁ energy of the **34CzBN** increased significantly compared to 44CzBN due to the interrupted π -conjugation by large dihedral angle. As a result, the ΔE_{ST} values of the CzBN, 34CzBN and 44CzBN were calculated to be 0.30 eV, 0.22 eV and 0.15 eV, respectively.



Fig. 4 a) Fluorescence spectra of the compounds collected using 10 wt% emitter doped DPEPO

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films and b) phosphorescence spectra of the compounds recorded at 77 k in frozen THF.

Fig. 5 Emission spectra of the compounds a) CzBN, b) 34CzBN and c) 44CzBN collected in different solvents (CH = cyclohexane, TOL = toluene, THF = tetrahydrofuran, MC = dichloromethane).

The TADF behavior of these materials was analyzed by transient PL measurements using 10 wt% emitter doped DPEPO films at room temperature (Figure 6). The **CzBN** displayed strong prompt with lifetime of 4.7 ns and very weak delayed fluorescence. The weak delayed component of **CzBN** could be attributed to its large ΔE_{ST} and inefficient RISC process. The **34CzBN** and **44CzBN** compounds showed clear prompt and delayed components with

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corresponding lifetimes of 6.6 ns/7.9 µs and 9.0 ns/5.8 µs, respectively. The delayed fluorescence component was unambiguously assigned to the thermal up-conversion of triplet excitons from T_1 to S_1 via RISC process followed by radiative transition from S_1 to S_0 . The relatively short delayed fluorescence lifetime (t_d) of 44CzBN is attributed to its small ΔE_{ST} . The absolute PLQY of the doped films was measured using an integrating sphere method under nitrogen at room temperature. The PLQYs of the compounds were 20% for CzBN, 58% for 34CzBN, 51% for 44CzBN. The superior PLOY of 34CzBN and 44CzBN compared to CzBN is attributed to the utilization of two channel emission process and efficient contribution of triplet excitons for light emission through RISC, which is evident from the high PLQY of delayed fluorescence component of 34CzBN (46%) and 44CzBN (40%) compared to CzBN (9%). The relatively high PLQY of 34CzBN compared to its isomer 44CzBN may be due to molecular rigidity by the sterically hindered carbazole unit in the biphenyl unit. Furthermore, RISC rate constants (K_{RISC}) of the materials were calculated using PLQY and transient PL data according to the literature procedure. The 34CzBN and 44CzBN showed K_{RISC} of 5.51 × 10⁵ s⁻¹ and 7.0 \times 10⁵ s⁻¹. These results indicate that the **34CzBN** and **44CzBN** have potential as TADF emitters.



Fig. 6 Transient PL decay profiles of the 10wt% emitter doped DPEPO films.

Electrochemical and Thermal Properties

The electrochemical behavior of these compounds was analyzed by cyclic voltammetry (CV) measurements in dilute dichloromethane solution using 0.1 M tetrabutylammonium perchlorate electrolyte. The corresponding HOMO and LUMO energy levels of the materials were determined from their onset potentials of oxidation and reduction waves relative to ferrocene (-4.80 eV) and were -5.87 eV and -2.92 eV for CzBN, -5.87 eV and -3.25 eV for 34CzBN and -5.84 eV and -3.29 eV for 44CzBN. The HOMO energy levels of the compounds were almost unchanged, whereas the LUMO levels of 34CzBN and 44CzBN were deeper than that of CzBN due to the increased number of cyano acceptor units in former compounds. The 44CzBN emitter exhibited relative small HOMO-LUMO gap owing to the increased π -conjugation between the two emitting units.

Thermal stability of the compounds was determined by thermogravimetric analysis (TGA) under nitrogen at a heating rate of 10 °C/min. The corresponding TGA traces are shown in Figure S1 and the data are tabulated in Table 1. The two materials exhibited marked thermal stability with high decomposition temperatures corresponding to 5% weight loss (T_d) of 448 °C for **34CzBN** and 485 °C for **44CzBN** compared to 354 °C of **CzBN**. The extended π -conjugation through small dihedral angle thermally stabilized the **44CzBN** molecule.

Compound	λ_{abs} , nm (ε_{max} , M ⁻	$\lambda_{\rm em}$ (nm),	$E_{\rm S}/E_{\rm T}$	$\Delta E_{\rm ST}$	HOMO/LUMO	$E_{\rm g}({\rm eV})^{\rm f}$	$t_{\rm p}/t_{\rm d}({\rm ns}/{\rm \mu s})^{\rm g}$	${m arphi}_{ m p}^{ m h} / {m arphi}_{ m d}^{ m i} / {m arphi}_{ m PL}^{ m j}$	Tonset
	$^{1} \text{ cm}^{-1} \times 10^{3})^{a}$	(film) ^b	(eV) ^c	(eV) ^d	(eV) ^e	ç	1		(°C) ^k
CzBN	350 (6.3), 332	403	3.40/3.10	0.30	5.87/2.92	2.95	4.7/-	0.11/0.09/0.20	354
	(13.4), 289 (32.3)								
34CzBN	364 (19.9), 331	453	3.18/2.96	0.22	5.87/3.25	2.62	6.6/7.9	0.12/0.46/0.58	448
	(41.0), 287 (93.7)								
44CzBN	392 (11.0), 316	490	2.95/2.80	0.15	5.84/3.29	2.55	9.0/5.8	0.11/0.40/0.51	485
	(sh), 289 (153.8)								

 Table 1. Photophysical, electrochemical and thermal data of the compounds

^aCollected in THF solution ^bCollected for 10wt% doped film in DPEPO. ^cCalculated from the onset of fluorescence and phosphorescence spectra. ^dCalculated singlet-triplet energy gap. ^eHOMO and LUMO estimated from the cyclic voltammograms. ^fElectrochemical band gap. ^gPrompt (t_p) and delayed (t_d) fluorescence lifetimes. ^hPrompt (Φ_p) and ⁱdelayed (Φ_d) PLQY determined from the total PLQY and the proportion of the integrated area of individual components in the transient PL spectra to the total integrated area. ^jAbsolute PLQY of the doped films in DPEPO measured using an integrating sphere under nitrogen atmosphere at room temperature. ^kTemperature corresponds to 5% weight loss (T_{onset})

Electroluminescence Properties

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To evaluate the electroluminescence (EL) performance of the emitters, we fabricated vacuum processed multilayer OLED devices by employing them as emitting dopants in the DPEPO host. The fabricated device configuration is as follows: ITO (50 nm)/PEDOT:PSS(60 nm)/TAPC(20 nm)/mCP(10)nm)/EML (25)nm:10 wt%)/TSPO1(5 nm)/TPBi(20 nm)/LiF(1.5)/Al(200 nm). Here, diphenylphosphine oxide-4-(triphenylsilyl)-Phenyl (TSPO1) used as electron transporting type exciton blocking layer, mCP used as hole transporting type exciton blocking layer. Di-[4-(N,N-ditolyl-amino)phenyl]cyclohexane (TAPC) and LiF served as hole transport and electron injection layers. The emitting layers (EML) were CzBN or 34CzBN or 44CzBN (10wt%) doped DPEPO layer. The device structure and energy level diagram of device are shown in Figure 7. The results of the device performance of the compounds including current density (J)-voltage (V)-luminance (L), external quantum efficiency (EQE) versus luminance plots, EL spectra and CIE 1931 color chromaticity diagram, are shown in Figure 8 and the final device parameters were summarized in Table 2.



Fig. 7 Device structure and energy level alignment of the materials.

The main objective of the two channel emission molecular design was to enhance the EQE and to control the emission color by managing the degree of conjugation through interconnection position engineering. As intended, the **34CzBN** device exhibited deep-blue emission with a peak maximum of 458 nm and CIE color coordinate of (0.14, 0.14), whereas

emission with a peak maximum of 458 nm and CIE color coordinate of (0.14, 0.14), whereas its structural isomer **44CzBN** showed green emission with a peak maximum of 500 nm and CIE color coordinate of (0.20, 0.44). The simple engineering of the interconnect position greatly changed the EL emission spectra by switching the conjugation channel. The deep-blue emission of **34CzBN** is attributed to the interrupted π -conjugation between the two emitting cores by their non-conjugative mode of connection. Also, the increased molecular rigidity of **34CzBN** with the interlocked carbazole unit in the biphenyl core sharpened the emission spectrum, resulting in small FWHM of 63 nm compared to 76 nm of its isomeric derivative **44CzBN**. The emission spectrum of **34CzBN** was even narrower than that of the **CzBN** (FWHM ~ 72 nm). The absence of any additional emission peaks in the EL spectra from the adjacent layers and the close resemblance of the EL spectra of the compounds with their PL spectra indicate the efficient exciton confinement and complete energy transfer from the host to dopant.

The maximum EQEs (EQE_{max}) of the **34CzBN** and **44CzBN** devices were 15.2 and 13.8% compared with 3.4% of the **CzBN** device. The **34CzBN** and **44CzBN** devices showed more than four-times higher EQE than the **CzBN** device. This is mainly attributed to the high PLQY through two channel emission process and fast RISC through small ΔE_{ST} of **34CzBN** and **44CzBN** compared to **CzBN**. In particular, the device performances of the **34CzBN** device is comparable to the reported deep blue TADF emitters with CIEy ≤ 0.15 .⁷⁻²⁸ The results demonstrate that the simple conjugation isolation strategy of the two channel emission based TADF emitters by careful interconnect position engineering is an effective approach to develop high EQE and deep-blue emitting TADF OLEDs.



Fig. 8 a) *I-V-L* plots, b) EQE *vs* luminance, c) EL spectra and d) CIE color chromaticity diagram of the devices.



Journal of Materials Chemistry C

Dopant	Voltage (V)	EQE (%)		Current efficiency (cd/A)		Power efficiency (lm/W)		EL peak	CIE (x, y)
		Max.	$@100 \text{ cd/m}^2$	Max.	$@100 \text{ cd/m}^2$	Max	@100 cd/m ²	(nm)/FWHM	
CzBN	4.4	3.4	0.6	1.4	0.3	1.1	0.1	426/72	0.16, 0.08
34CzBN	4.3	15.2	7.3	17.4	8.5	12.1	4.4	458/63	0.14, 0.14
44CzBN	4.4	13.8	9.1	35.2	22.8	26.6	11.7	500/76	0.20, 0.44

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Conclusion

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In conclusion, we developed two TADF emitters, **34CzBN** and **44CzBN**, with different degree of conjugation by directly coupling two identical TADF units through different interconnect positions. The change of the interconnection position controlled the degree of conjugation and managed emission properties of the TADF emitters. The non-conjugative mode of connection in **34CzBN** limited the extensive conjugation and enabled deep blue emission. Whereas, the extended conjugation of **44CzBN** witnessed green emission. Two-channel emission process of **34CzBN** and **44CzBN** benefited more than four-fold improved device performance with EQE_{max} of 15.2% and 13.8% compared to single channel emission process in **CzBN** (3.4%). Therefore, we believe that our results provide fundamental insights to design two channel emission based TADF emitters over a wide color gamut with uncompromised EQE.

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References

 a) C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.* 1987, **51**, 913; b) Y. Chi and P. T. Chou, *Chem. Soc. Rev.* 2010, **39**, 638; c) X. L. Guo, H. Li, W. Nie, S. Luo, S. Gan, R. Hu, A. Hu, Z.
 Qin, S. Zhao, S. J. Su and B. Z. Tang, *Adv. Funct. Mater.* 2017, **27**, 1606458; d) P. Rajamalli,
 N. Senthilkumar, P. Y. Huang, C. C. R. Wu, H. W. Lin and C. H. Cheng, *J. Am. Chem. Soc.* 2017, **139**, 10948; e) H. Tsujimoto, D. G. Ha, G. Markopoulos, H. S. Chae, M. A. Baldo and T. M. Swager, *J. Am. Chem. Soc.* 2017, **139**, 4894; f) Y. Zhang, Y. Wang, J. Song, J. Qu, B.

Li, W. Zhu, W. Y. Wong, *Adv. Optical Mater.* 2018, **6**, 1800466; g) R. Sharma, D. Volyniuk,
C. Popli, O. Bezvikonnyi, J. V. Grazulevicius and R. Misra, *J. Phys. Chem. C*, 2018, **122**, 15614; h) W. C. Chen, Y. Yuan, Z. L. Zhu, Z. Q. Jiang, S. J. Su, L. S. Liao and C. S. Lee, *Chem. Sci.* 2018, **9**, 4062; i) A. Maheshwaran, V. G. Sree, H. Y. Park, H. Kim, S. H. Han, J.
Y. Lee and S. H. Jin, *Adv. Funct. Mater.* 2018, **28**, 1802945; j) X. Wang, S. Wang, J. Lv, S.
Shao, L. Wang, X. Jing, F. Wang, *Chem. Sci.* 2019, **10**, 2915; k) Y. Liu, C. Li, Z. Ren, S. Yan
and M. R. Bryce, *Nat. Rev. Mater.* 2018, **3**, 18020; l) T. Shan, Y. Liu, X. Tang, Q. Bai, Y. Gao,
Z. Gao, J. Li, J. Deng, B. Yang, P. Lu and Y. Ma, *ACS Appl. Mater. Interfaces*, 2016, **8**, 28771;
m) L. Yu, Z. Wu, G. Xie, C. Zhong, Z. Zhu, D. Ma and C. Yang, *Chem. Commun.* 2018, **54**, 1379.

 Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang and W. Huang, *Adv. Mater*, 2014, 26, 7931; b) Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z.
 Chi and M. P. Aldred, *Chem. Soc. Rev.* 2017, 46, 915; c) Y. Im, M. Kim, Y. J. Cho, J. A. Seo,
 K. S. Yook and J. Y. Lee, *Chem. Mater.* 2017, 29, 1946; d) M. Y. Wong and E. Z. Colman, *Adv. Mater.* 2017, 29, 1605444; e) X. Cai and S. J. Su, *Adv. Funct. Mater.* 2018, 28, 1802558; f) Y. Im, S. Y. Byun, J. H. Kim, D. R. Lee, C. S. Oh, K. S. Yook and J. Y. Lee, *Adv. Funct. Mater.* 2017, 27, 1603007; g) T. Chatterjee and K. T. Wong, *Adv. Optical Mater.* 2019, 7, 1800565; h) M. Godumala, S. Choi, M. J. Cho and D. H. Choi, *J. Mater. Chem. C*, 2016, 4, 11355; h) Y. Zou, S. Gong, G. Xie and C. Yang, *Adv. Optical Mater.* 2018, 6, 1800568; i) T.
 Huang, W. Jiang and L. Duan, *J. Mater. Chem. C*, 2018, 6, 5577; j) R. K. Konidena and J. Y.
 Lee, *Chem. Rec.* 2018, DOI: 10.1002/tcr.201800136; k) Q. Wei, N. Fei, A. Islam, T. Lei, L.
 Hong, R. Peng, X. Fan, L. Chen, P. Gao and Z. Ge, *Adv. Optical Mater.* 2018, 6, 1800512; l)
 P. L. D. Santos, J. S. Ward, D. G. Congrave, A. S. Batssanov, J. Gng, J. E. Stacey, T. J. Penfold,
 A. P. Monkman and M. R. Bryce, *Adv. Sci.* 2018, 5, 1700989; m) Y. T. Lee, P. C. Tseng, T.
 Komino, M. Mamada, R. J. Ortiz, M. L. Leung, T. L. Chiu, C. F. Lin, J. W. Lee, C. Adachi, C.

Journal of Materials Chemistry C Accepted Manuscrip

T. Chen and C. T. Chen, ACS Appl. Mater. Interfaces. 2018, 10, 43842.

3. a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S.
R. Forrest, *Nature*, 1998, **395**, 151; b) C. Adachi, M. A. Baldo and S. R. Forrest, *App. Phys. Lett.* 2000, **77**, 904; c) Y. F. Zhang, J. Lee and S. R. Forrest, *Nat. Commun.* 2014, **5**, 5008; d)
D. Ma, T. Tsuboi, Y. Qiu and L. Duan, *Adv. Mater.* 2017, **29**, 1603253; e) A. K. W. Chan, M.
Ng, Y. C. Wong, M. Y. Chan, W. T. Wong and V. W. W. Yam, *J. Am. Chem. Soc.* 2017, **139**, 10750.

4. a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, 492, 234; b)
Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka and C. Adachi, *Nature Photonics*, 2014, 8,
326; c) I. S. Park, H. Komiyama and T. Yasuda, *Chem. Sci.* 2017, 8, 953; d) X. Li, Y. Z. Shi,
K. Wang, M. Zhang, C. J. Zheng, D. M. Sun, G. L. Dai, X. C. Fan, D. Q. Wang, W. Liu, Y. Q.
Li, J. Yu, X. M. Ou, C. Adachi and X. H. Zhang, *ACS Appl. Mater. Interfaces*, 2019, 11, 13472;
e) X. Fan, C. Li, Z. Wang, Y. Wei, C. Duan, C. Han and H. Xu, *ACS Appl. Mater. Interfaces*, 2019, 11, 4185; f) Z. Chen, Z. Wu, F. Ni, C. Zhong, W. Zeng, D. Wei, K. An, D. Ma and C. Yang, *J. Mater. Chem. C*, 2018, 6, 6543; g) Y. Liu, G. Xie, K. Wu, Z. Luo, T. Zhou, Z. Zeng,
J. Yu, S. Gong and C. Yang, *J. Mater. Chem. C*, 2016, 4, 4402.

5. a) D. R. Lee, M. Kim, S. K. Jeon, S. H. Hwang, C. W. Lee, J. Y. Lee, *Adv. Mater.* 2015, 27,
5861; b) K. J. Kim, G. H. Kim, R. Lampande, D. H. Ahn, J. B. Im, J. S. Moon, J. K. Lee, J. Y. Lee, J. Y. Lee and J. H. Kwon, *J. Mater. Chem. C*, 2018, 6, 1343; c) S. Hirata, Y. Sakai, K. Masui, H. Tanaka, S. Y. Lee, H. Nomura, N. Nakamura, M. Yasumatsu, H. Nakanotani, Q. Zhang, K. Shizu and H. Miyazaki, C. Adachi, *Nat. Mater.* 2015, 14, 330; d) J. J. Liang, Y. Li, Y. Yuan, X. D. Zhu, S. Barlow, M. K. Fung, Z. Q. Jiang, S. R. Marder, L. S. Liao, *Mater. Chem. Front.* 2018, 2, 917.

6. a) Y. J. Cho, S. K. Jeon, B. D. Chin, E. Yu and J. Y. Lee, *Angew. Chem. Int. Ed.* 2015, 54, 5201; b) M. Kim, S. K. Jeon, S. H. Hwang, S. S. Lee, E. Yu and J. Y. lee, *Chem. Comm.* 2016,

- **52**, 339; c) D. Wei, F. Ni, Z. Wu, Z. Zhu, Y. Zou, K. Zheng, Z. Chen, D. Ma and C. Yang, *J. Mater. Chem. C*, 2018, **6**, 11615.
- 7. M. Y. Wong, S. Krotkus, G. Copley, W. Li, C. Murawski, D. Hall, G. J. Hadley, M. Jaricot,
- D. B. Cordes, A. M. Z. Slawin, Y. Oliver, D. Beljonne, L. Muccioli, M. Moral, J. C. S. Garcia,

M. C. Gather, I. D. W. Samuel and E. Z. Colman, ACS Appl. Mater. Interfaces, 2018, 10, 33360.

- 8. Q. Zhang, J. Li, K. Shizu, S. Huang, S. Harita, H. Miyazaki and C. Adachi, *J. Am. Chem. Soc*, 2012, **134**, 14706.
- M. Liu, Y. Seino, D. Chen, S. Inomata, S. J. Su, H. Sasabe and J. Kido, *Chem. Commun.*2015, 51, 16353.
- 10. I. Lee and J. Y. Lee, Organic Electron. 2016, 29, 160.
- 11. J. W. Sun, J. Y. Baek, K. H. Kim, J. S. Huh, S. K. Kwon, Y. H. Kim and J. J. Kim, *J. Mater. Chem. C*, 2017, **5**, 1027.

T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y.
 Ono and T. Ikuta, *Adv. Mater.* 2016, 28, 2777.

13. K. Matsui, S. Oda, K. Yoshiura, K. Nakajima, N. Yasuda and T. Hatakeyama, J. Am. Chem. Soc. 2018, 140, 1195.

 L. S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani and C. Adachi, *Angew. Chem. Int. Ed.* 2017, 56, 1571.

15. Y. Wada, S. Kubo and H. Kaji, Adv. Mater. 2018, 30, 1705641.

16. S. J. Woo, Y. Kim, M. J. Kim, J. Y. Baek, S. K. Kwon, Y. H. Kim and J. J. Kim, *Chem. Mater.* 2018, **30**, 857.

17. R. Komatsu, T. Ohsawa, H. Sasabe, K. Nakao, Y. Hayasaka and J. Kido, *ACS Appl. Mater. Interfaces*, 2017, **9**, 4742.

18. Y. H. Lee, S. Park, J. Oh, J. W. Shin, J. Jung, S. Yoo and M. H. Lee, ACS Appl. Mater.

Journal of Materials Chemistry C Accepted Manuscrip

View Article Online DOI: 10.1039/C9TC02618E

C. Y. Chan, L. S. Cui, J. U. Kim, H. Nakanotani and C. Adachi, *Adv. Funct. Mater.* 2018,
 28, 1706023.

- 20. N. Jurgensen, A. Kretzschmar, S. Hofle, J. Freudenberg, U. H. F. Bunz and G. H. Sosa, *Chem. Mater.* 2017, **29**, 9154.
- 21. W. Huang, M. Einzinger, T. Zhu, H. S. Chae, S. Jeon, S. G. Ihn, M. Sim, S. Kim, M. Su,
 G. Teverovskiy, T. Wu, T. V. Voorhis, T. M. Swager, M. A. Baldo and S. L. Buchwald, *Chem. Mater.* 2018, **30**, 1462.
- 22. T. L. Wu, S. H. Lo, Y. C. Chang, M. J. Huang and C. H. Cheng, *ACS Appl. Mater. Interfaces*, 2019, **11**, 10768.
- 23. M. Yokoyama, K. Inada, Y. Tsuchiya, H. Nakanotani and C. Adachi, *Chem. Commun.* 2018, 54, 8261.
- 24. K. Matsuo and T. Yasuda, Chem. Commun. 2019, 55, 2501.
- 25. Y. J. Cho, S. K. Jeon, S. H. Lee, E. Yu and J. Y. Lee, Chem. Mater. 2016, 28, 5400.
- 26. Q. Zhang, S. Xiang, Z. Huang, S. Sun, S. Ye, X. Lv, W. Liu, R. Guo and L. Wang, *Dyes Pigm.* 2018, **115**, 51.
- 27. Y. Im, S. H. Han and J. Y. Lee, J. Mater. Chem. C, 2018, 6, 5012.
- S. J. Woo, Y. Kim, S. K. Kwon, Y. H. Kim and J. J. Kim, ACS Appl. Mater. Interfaces, 2019, 11, 7199.
- 29. R. K. Konidena, K. H. Lee and J. Y. Lee, Chem. Asian. J. 2019, 14, 313.
- 30. N. Miyaura, K. Yamada and A. Suzuki, Tetrahedron Lett., 1979, 20, 3437.

31. R. K. Konidena, K. R. J. Thomas, A. Pathak, D. K. Dubey, S. Sahoo and J. H. Jou, *ACS Appl. Mater. Interfaces*, 2018, **10**, 24013.



