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Enhancing performance for blue TADF emitters by introducing intramolecular CH···N hydrogen bonding between donor and acceptor

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Abstract: Three novel thermally activated delayed fluorescence (TADF) emitters, named MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM are designed and synthesized for fabricating blue emission devices. The position of nitrogen atom in pyridine ring is varied relative to the donor unit and the presence of CH···N hydrogen bonding in MCZ-P3-DTM is confirmed by theoretic simulation and ¹H NMR analysis. Due to the introduction of CH···N hydrogen bonding between donor and acceptor, the dihedral angles, photophysical properties, together with thermal stabilities, of the targeted compounds are regulated ingeniously. As a consequence, MCZ-P3-DTM displays an increase of the molar extinction coefficient obviously and offers a higher PLQY of 60.1%. The TADF device adopting MCZ-P3-DTM as emitter shows a maximum external quantum efficiency (EQE) of 12.1%, which is superior to those of MCZ-B-DTM and MCZ-P2-DTM, demonstrating the introducing of intramolecular hydrogen bonding interactions between donor and acceptor is an efficient strategy for future structural design of TADF emitters.

Keywords: intramolecular hydrogen bonding; high absorption coefficient; blue emission; TADF

1. Introduction

Organic light emitting diodes (OLEDs) are drawing tremendous attention due to their various advantages such as light weight, flexibility and quick response, have become the most promising technology in the new-generation display field[1-7]. Under electrical excitation, conventional fluorescent OLEDs can only harvest singlet excitons for light emitting, therefore limiting the internal quantum efficiency (IQE) to 25%. The phosphorescent materials can harvest both singlet and triplet excitions through intersystem crossing (ISC) process by heavy atom effect to realize 100% IQE

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[8-10]. However, the incorporation of noble metals has many disadvantages like cost, environmental pollution and instability, limiting their extensive application. Recently, TADF emitters can harvest both triplet and singlet excitons through reverse intersystem crossing (RISC) process under thermal activation, have been considered as a cheaper alternative to phosphorescent OLEDs for the next generation display. The principle of design TADF molecule is separating the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule, and therefore the energy gap between T_1 and S_1 was narrowed to facilitate the triplet excitons up-convert to singlet ones[11-19].

Generally, the TADF emitters are designed to employ a twist structure between donor and acceptor for separating the HOMO and LUMO to achieve the minimum $\Delta E_{st}[20, 21]$. In the past few years, there are numerous high-efficiency TADF emitters with skillfully selected donor and acceptor units adopting D-A structures have been developed[22-24]. However, the twist structure between donor and acceptor with limited orbital overlap often leads to a weak absorption along with a low photoluminescence quantum yield (PLQY)[25, 26]. Hence, the method to develop TADF emitters with requisite small ΔE_{st} , intensive absorption and high PLQY is essential for high-performance OLEDs. To address these issues, increasing the rigidity of the molecule is a valid way to obtain desirable quantum efficiencies. Thereby, several molecular design means for increasing rigidity have already been exploited to improve the device efficiency: (i) connecting dual emitting cores to form steric hindrance[27, 28]; (ii) introducing steric methyl between donor and acceptor moiety to enhance steric hindrance[29-31]; (iii) increasing molecular rigidity through ortho position linkage between donor and acceptor units[32-34]. In addition to the above means, incorporating hydrogen bonding interaction into the molecule structure also seems to a concise and effective way to generate rigid molecule structure[35, 36]. Moreover, intramolecular hydrogen bonding interaction can restrict the rotation between donor and acceptor to inhibit non-radiative transition process and enlarge conjugation[37], resulting in high absorption coefficient and improved PLQY of the TADF emitters.

Based on the aforementioned strategy, three novel TADF molecules, 4-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)phenyl)(dibenzo[b,d]thiophen-2-yl)m ethanone (MCZ-B-DTM),

5-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)pyridin-2-yl)(dibenzo[b,d]thiophen-2yl)methanone (MCZ-P2-DTM),

6-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)pyridin-3-yl)(dibenzo[b,d]thiophen-2yl)methanone (MCZ-P3-DTM) were designed and synthesized. In these three compounds, the 3,6-bis(4-methoxyphenyl)-9H-carbazole is chosen as the donor moiety due to its moderate donor ability which is suitable for constructing blue TADF emitters. Comparative study of their thermal stabilities, photophysical properties and device performances are carried out in detail. Because of the different position of pyridine group connecting to the keto and carbazole derivatives, intramolecular CH···N hydrogen bonding between donor and acceptor formed in MCZ-P3-DTM is confirmed by theoretical simulation and ¹H NMR analysis. Compared with MCZ-B-DTM and MCZ-P2-DTM, MCZ-P3-DTM exhibits reduced dihedral angle with increased absorption coefficient, thermal stability and PLQY. As a result, MCZ-P3-DTM based sky-blue OLED achieves external quantum efficiency (EQE) of 12.1%.

2. Experimental

2.1 General information

All solvents and materials were purchased from commercial sources and used without any further purification if not specifically mentioned. ¹H NMR and ¹³C NMR spectra were measured on a Bruker Advance 600MHz using Si(CH₃)₄ as internal standard. Molecular masses were recorded on a LC-MS (Agilent 1260, Agilent Technologies), UV-Vis absorption spectra and photoluminescence emission spectra of the target compounds were measured on a UV-2600 (Shimadzu Corporation) and a Fluoromax-4 (Horiba Jobin Yvon Inc) spectrophotometer, respectively. The solid PL

quantum efficiency was obtained using Fluoromax-4 (Horiba Jobin Yvon Inc) with an integrating sphere under nitrogen at room temperature. Thermo gravimetric analysis (TGA) were performed with Netzsch simultaneous thermal analyzer (STA) system (STA409 PC) under a dry nitrogen gas flow at a heating rate of 10° C min⁻¹. Differential scanning calorimetry (DSC) curves were measured using a Netzsch instrument (TA, Netzsch). Cyclic voltammogram was measured on CH Instruments, Inc (Shanghai, China) 660E electrochemical work station in a solution of Bu₄NClO₄ (0.1 M) in anhydrous acetonitrile at a scan rate of 50 mV s⁻¹ with a Pt wire and Ag/AgCl electrodes as the counter electrode and the reference electrode, respectively. The ferrocene was selected as internal standard and the molecule thin films coated on ITO-coated glass were measured.

2.2 Device measurements and characterization

The glasses coated by indium tin oxide (ITO) with sheet resistance of 15 Ω per square were cleaned with deionized water, acetone and ethanol for 15 minutes in sequence before fabricating devices. Then the substrates were treated with UV-Ozone for 20 minutes. Organic layers were deposited into the ITO-coated substances when the pressure reached ~ 4 × 10⁻⁴ Pa in vacuum chamber. The deposition rates of functional layers were 1~2 Å s⁻¹, 0.1 Å s⁻¹ and 6 Å s⁻¹ for organic materials, LiF and Al, respectively. The active area was 3 × 3 mm⁻² controlled by a shadow mask. All the tests were performed at room temperature in ambient condition. Current density and luminance versus driving voltage curves and electroluminescent spectra were measured by Keithley2400s Source Meter and Photo Research PR 655 spectrophotometer. External quantum efficiencies of the devices were calculated assuming a Lambertian emission distribution.

2.3 Materials

2.3.1 Synthesis of (6-bromopyridin-3-yl)(dibenzo[b,d]thiophen-2-yl)methanone (5Br-DTM)

5-bromonicotinic acid (1.5 g, 5.36 mmol) was dissolved in thionyl chloride (15 mL) and refluxed for 3 h. Then, the excess thionyl chloride was removed under vacuum to give 5-bromopicolinoyl chloride as yellow crystalline solid. Next, 5-bromonicotinoyl chloride and dibenzothiophene (0.99 g, 5.36 mmol) were dissolved in dry dichloromethane (30 ml), and then aluminum trichloride (0.85 g, 6.4 mmol) was added slowly at 0°C followed by stirring at room temperature for 6 h and refluxed for 3 h. Then, the reaction mixture was quenched through pouring into 200 mL ice-HCl solution and extracted with dichloromethane for three times. The combined organic phase was washed three times with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified on a silica gel column using petroleum ether/dichloromethane mixture (4:1, v/v) as eluent to afford the product as yellow powder in 57% yield. ¹H NMR (600 MHz, DMSO-*d*6) δ [ppm]: 8.97-8.91 (m, 2H), 8.96-8.92 (m, 2H), 8.48 (d, J = 7.1 Hz, 1H), 8.48 (d, J = 7.1 Hz, 1H), 8.39 (dd, J = 8.3, 2.3 Hz, 1H), 8.39 (dd, J = 8.3, 2.3 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.13-8.07 (m, 2H), 8.12-8.08 (m, 2H), 8.03 (dd, J = 8.4, 0.5 Hz, 1H), 7.57 (dtd, J = 21.4, 7.2, 1.2 Hz, 2H). ¹³C NMR (151 MHz, DMSO) δ [ppm]: 192.73, 153.70, 150.00, 144.29, 140.86, 139.38, 135.17, 135.14, 132.89, 129.04, 128.21, 126.55, 125.68, 125.19, 124.41, 123.73, 123.38, 123.00. MS (LC-MS) [m/z]: calcd for C₁₈H₁₀BrNO₅, 366.97; found, 367.96.

2.3.2 Synthesis of (5-bromopyridin-2-yl)(dibenzo[b,d]thiophen-2-yl)methanone (6Br-DTM)

6Br-DTM was prepared via the same procedure to that of 5Br-DTM by using 6-bromopicolinic acid (1.2 g, 2.8 mmol) instead of 5-bromonicotinic acid in 54% yield.

¹H NMR (600 MHz, CDCl₃) δ [ppm]: 8.85 (dd, J = 2.4, 0.6 Hz, 1H), 8.59 (d, J = 1.4 Hz, 1H), 8.22-8.19 (m, 1H), 8.16 (dd, J = 8.2, 2.4 Hz, 1H), 8.01-7.98 (m, 1H), 7.92 -7.88 (m, 2H), 7.54 (qd, J = 6.8, 1.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ [ppm]: 193.26, 154.97, 151.10, 145.16, 139.90, 139.78, 135.77, 134.88, 132.81, 132.40,

127.76, 127.69, 125.10, 124.44, 123.49, 123.05, 123.03, 122.03. MS (LC-MS) [m/z]: calcd for C₁₈H₁₀BrNO₅, 366.97; found, 366.80.

2.3.3 Synthesis of (4-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)phenyl) (dibenzo[b,d]thiophen-2-yl)methanone (MCZ-B-DTM)

3,6-bis(4-methoxyphenyl)-9H-carbazole (758.9 mg, 2.0 mmol) and sodium hydride (60%, 72 mg, 3 mmol) were dissolved in dry DMF (15 ml) under nitrogen condition. After 30 stirring min at room temperature, dibenzo[b,d]thiophen-2-yl(4-fluorophenyl)methanone (500 mg, 1.63 mmol) in dry DMF (5 ml) was added, and then the reaction mixture was stirred at 110°C for 12 h. After cooling, adding cold water to the mixture slowly and extracted with dichloromethane for three times. The solvent was removed under reduced pressure and the residue was purified on a silica gel column using petroleum ether/dichloromethane mixture (3:1, v/v) as eluent to afford the product as yellow-green powder in 78% yield. ¹H NMR (600 MHz, CDCl₃) δ [ppm]: 8.73 (s, 1H), 8.35 (d, J = 1.6 Hz, 2H), 8.29-8.26 (m, 1H), 8.16 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 1.0 Hz, 2H), 7.94-7.91 (m, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.69-7.66 (m, 6H), 7.62 (d, J = 8.5 Hz, 2H), 7.56-7.53 (m, 2H), 7.06-7.03 (m, 4H), 3.89 (s, 6H). ¹³C NMR (151 MHz. CDCl3) & [ppm]: 195.35, 158.83, 144.33, 141.69, 139.78, 136.32, 135.64, 135.14, 134.31, 133.99, 133.80, 131.97, 128.30, 128.12, 127.56, 126.13, 125.59, 124.98, 124.55, 123.57, 123.01, 122.72, 122.08, 118.52, 114.30, 110.17, 55.41. MS (LC-MS) [m/z]: calcd for C₄₅H₃₁NO₃S, 665.20; found, 666.80.

2.3.4 synthesis of (6-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)pyridin-3-yl) (dibenzo[b,d]thiophen-2-yl)methanone (MCZ-P2-DTM)

3,6-bis(4-methoxyphenyl)-9H-carbazole (618.6 mg, 1.63 mmol), 5Br-DTM (500 mg, 1.36 mmol), sodium carbonate (18.8 mg, 0.136 mmol), Copper iodide(25.9 mg, 0.136 mmol), and 1,10-phenanthroline (24.5 mg, 0.136 mmol) were dissolved in dry DMF (20 ml), the mixture stirred at 160°C for 12 h. After cooling, the mixture was

poured into water and extracted with dichloromethane for three times. The solvent was removed under reduced pressure and the residue was purified on a silica gel column using petroleum ether/dichloromethane mixture (3:1, v/v) as eluent to afford the product as yellow powder in 76% yield. ¹H NMR (600 MHz, CDCl₃) δ [ppm]: 9.13 (d, J = 2.2 Hz, 1H), 9.07 (d, J = 1.2 Hz, 1H), 8.46 (d, J = 8.3 Hz, 1H), 8.37-8.32 (m, 3H), 8.27 (ddd, J = 10.7, 7.1, 2.7 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 6.0, 3.0 Hz, 1H), 7.71-7.65 (m, 6H), 7.60 (d, J = 8.5 Hz, 2H), 7.53 (dd, J = 5.9, 3.1 Hz, 2H), 7.05 (d, J = 8.7 Hz, 4H), 3.89 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ [ppm]: 192.12, 158.94, 153.08, 146.07, 144.85, 139.66, 139.49, 137.17, 135.52, 135.37, 134.62, 134.19, 134.05, 132.61, 129.08, 128.32, 127.39, 126.16, 125.86, 124.90, 124.89, 124.75, 122.94, 122.47, 122.09, 118.69, 114.33, 109.78, 55.42. MS (LC-MS) [m/z]: calcd for C₄₄H₃₀N₂O₃S, 666.20; found, 667.40.

2.3.5 synthesis of (5-(3,6-bis(4-methoxyphenyl)-9H-carbazol-9-yl)pyridin-2-yl) (dibenzo[b,d]thiophen-2-yl)methanone (MCZ-P3-DTM)

MCZ-P3-DTM was prepared via the same procedure to that of MCZ-P2-DTM by using 6Br-DTM (500 mg, 1.36 mmol) instead of 5Br-DTM in 73% yield.

¹H NMR (600 MHz, CDCl₃) δ [ppm]: 9.20 (d, J = 2.0 Hz, 1H), 8.72 (d, J = 0.9 Hz, 1H), 8.47 (d, J = 2.4 Hz, 1H), 8.32 (d, J = 1.7 Hz, 2H), 8.28-8.25 (m, 1H), 8.12 (d, J = 8.6 Hz, 2H), 8.05-8.00 (m, 2H), 7.93-7.89 (m, 2H), 7.71-7.67 (m, 6H), 7.54 (ddd, J = 7.0, 5.0, 1.6 Hz, 2H), 7.05-7.03 (m, 4H), 3.89 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ [ppm]: 157.95, 150.49, 138.97, 137.59, 134.13, 134.01, 133.06, 127.28, 126.83, 126.65, 124.78, 124.73, 124.03, 122.46, 122.01, 121.96, 121.06, 117.24, 116.12, 113.31, 111.36, 54.40. MS (LC-MS) [m/z]: calcd for C₄₄H₃₀N₂O₃S, 666.20; found, 667.40.



Scheme 1. Synthetic routes of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes and chemical structures of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM were illustrated in **Scheme 1**. The MCZ[38] and CP-BP-F[39] were obtained according to the previous literature methods. The key intermediates 5Br-DTM and 6Br-DTM were facilely prepared through Friedel-Crafts reactions. The target compounds were synthesized using MCZ reacted with corresponding intermediates by means of Ullmann coupling reactions. The final products were purified through column chromatography before measurements and device fabrication processes. The chemical structures of these three TADF emitters were confirmed by ¹H NMR, ¹³C NMR and mass spectrometry.

¹H NMR chemical shifts of the carbazole unit were influenced by the surrounding environment toward the molecule structures. As shown in **Figure S1**, when the carbazole unit was linked with phenyl in MCZ-B-DTM, the proximal proton of carbazole unit appeared at δ 7.63 ppm. However, when the phenyl was replaced by pyridine in MCZ-P3-DTM, the proton was shift to δ 8.47 by 0.84 ppm, which was due to the introduction of intramolecular CH···N bonding between the carbazole unit and pyridine moiety. Besides, there was no obvious CH···N bonding between donor and acceptor was found in MCZ-P2-DTM due to the nitrogen in pyridine ring was para to the carbazole unit, and therefore the proximal proton signal occurred at δ 7.61 ppm, which was similar to MCZ-B-DTM[35].

3.2. Thermal analysis

In order to analyze the thermal properties of designed emitters, the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a heating rate of 10° C min⁻¹ under nitrogen atmosphere. As shown in **Figure 1(c)**, all the compounds exhibited high decomposition temperatures (T_d, corresponding to 5% weight loss of initial value) around 400 to 434°C. Particularly, MCZ-P3-DTM presented a T_d at 434°C, which was higher than MCZ-B-DTM and MCZ-P2-DTM due to the increased rigidity by incorporating intramolecular hydrogen bonding. The higher decomposition temperatures implied their outstanding thermal stabilities, which mean that they were suitable for evaporation process during device fabrication. Meanwhile, the glass transition temperature (T_g) of the three emitters were not detected from 25 to 200°C, which was beneficial to reduce the phase separation rate of the host-gust system to form stable uniform films[40].

Compound	T_{g}^{a}/T_{d}^{a} [°C]	λ _{abs} ^b [nm]	λ _{em} ° [nm]	Φ _F ° [%]	τ_p^{d}/τ_d^{d} [ns]/[µs]	$S_1/T_1/\Delta E_{st}^e$ [eV]	HOMO/LUMO ^f [eV]
MCZ-B-DTM	- /400.0	292,366	462	35.6	7.8/5.1	3.14/2.71/0.43	5.38/2.42
MCZ-P2-DTM	- /428.6	292,390	493	51.4	8.4/3.5	2.91/2.55/0.23	5.44/2.59
MCZ-P3-DTM	- /434.2	292,382	484	60.1	5.9/4.2	2.98/2.69/0.29	5.42/2.50

Table 1. Thermal and photophysical properties.

^aMeasured by DSC/TGA at a heating rate of 10° C min⁻¹.

^bMeasured in toluene.

^cMeasured in thin films doped in mCP .

^dThe prompt and delayed fluorescence lifetimes of the emitters doped in mCP (10%) under room temperature. ^eObtained in toluene at 77 K.

^fHOMO was obtained from the CV: HOMO = $-(E_{onset}^{OX} + 4.8 - E_{1/2, \text{ ferrocene}}) \text{ eV}$, ferrocene was used as an external reference for calibration ($E_{1/2, \text{ ferroence}} = +0.45 \text{ eV} vs. \text{ Ag/AgCl})$ in Bu₄NClO₄/CH₃CN; LUMO = HOMO + E_{g}^{opt} .

3.3. Photophysical properties

The photophysical properties of these three compounds were collected based on UV-vis absorption, photoluminescence (PL) spectra and time-resolved transient PL, as presented in Figure 1 (a), (b) and (d). Their photophysical data were-summarized in **Table 1.** MCZ-P3-DTM displayed an absorption coefficient of 5.75×10^4 M⁻¹ cm⁻¹, which was higher than those of MCZ-B-DTM (4.95×10^4 M⁻¹ cm⁻¹) and MCZ-P2-DTM (4.44×10^4 M⁻¹ cm⁻¹), respectively. As anticipated for the molecular design, the absorption coefficient was intensified due to the more planar molecular structure with enhanced conjugation between donor and acceptor by introducing intramolecular CH ... N hydrogen bonding. Moreover, all the compounds showed two types absorption band. The absorption located on 298 nm can be ascribed to the local excited transition of their conjugated backbone, while broad absorption at the region of 366-390 nm were ascribed to intramolecular charge-transfer transition (ICT) from donor to acceptor units. In addition, the fluorescence emission maximum of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM were 463, 493 and 484 nm in toluene, respectively. Compared with the parent MCZ-B-DTM, the observed bathochromic shifts of MCZ-P2-DTM and MCZ-P3-DTM can be attributed to the enhanced ICT effect, which was resulted from the increased electron-withdrawing capacity of the acceptors through introducing additional pyridine. The PL of these compounds were also measured in different solvents with different polarities which displayed gradual red-shift from toluene (Tol) to N,N-dimethylformamide (DMF) (Figure S3 (a), (b) and (c)), indicating the electronic communication between the donor and acceptor moiety toward solvatochromic effect[41]. As shown in Figure S3 (d), the phosphorescence spectra at 77 K in toluene were obtained, the triplet energies can be calculated from the highest peak of the emission. The S_1/T_1 were 3.14/2.71, 2.91/2.55 and 2.98/2.69 eV of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM respectively. Therefore, the ΔE_{st} were 0.43, 0.23 and 0.29 eV for MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM, respectively. Notable, the energy gaps between singlet and triplet of MCZ-P2-DTM and MCZ-P3-DTM were smaller than

MCZ-B-DTM due to the enhanced coupling between singlet and triplet after introducing heteroatoms into the acceptor part.[42]. Moreover, the lower ΔE_{st} was beneficial for the effective RISC process from triplet to singlet states.



Figure 1. Absorption (a) and fluorescence (b) spectra of these compounds in 2.0×10^{-5} M toluene at room temperature (inset: photograph of PL spectra of the emitters in toluene under UV irradiation at 365 nm). (c) TGA and DSC (inset) curves of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P2-DTM. (d) Transient PL decay curves of 10 wt% emitter doped mCP thin films.

In order to testify the TADF characteristics of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM, the transient PL decay of 10 wt% emitter doped mCP thin films were measured under nitrogen. **Figure 1** (d) displayed the transient PL decay of the compounds and all of them exhibited bi-exponential decays. The fast decays were originated from the prompt fluorescence with short lifetimes of 7.8 ns, 8.4 ns and 5.9 ns, respectively. The slow decays can be attributed to delayed fluorescence with long lifetimes of 5.1 µs, 3.5 µs and 4.2 µs, respectively. Besides, as showed in **Figure S2**, the transient PL decays of neat films were measured for certifying the TADF characteristics. Similar to the doped films, all the compounds in neat films also displayed bi-exponential decay including fast and slow decays. The fast and slow decays of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM were 7.5 ns/2.1 µs,

8.2ns/2.9 µs and 6.8 ns/2.6 µs, respectively. The transient PL decay of 10 wt% emitter doped mCP thin films were also measured under different temperatures to further certify their TADF characters. As can be seen from the **Figure S4**, the delayed components increased gradually from 200 K to 300 K, suggesting that these compounds displayed obvious TADF characteristics and can be applied as TADF emitters. The time-resolved photoluminescence spectra of the TADF emitters in toluene under nitrogen at room temperature were measured. As shown in **Figure 2**, the prompt and delayed photoluminescence spectra were obtained with similar shapes which identified the delayed emission stemmed from the singlet via reversed process.



Figure 2. Prompt and delayed photoluminescence spectra of MCZ-B-DTM (a), MCZ-P2-DTM (b) and MCZ-P3-DTM (c) in toluene under nitrogen at room temperature.

For further exploring the emissive characteristics of the designed TADF emitters, the absolute PL quantum yield (PLQY) of the 10 wt% emitter doped mCP thin films were obtained through integrating sphere under nitrogen at room temperature. The PLQY of the doped thin films were 35.6%, 51.4% and 60.1% of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM, respectively. The MCZ-P3-DTM exhibited the higher PLQY among these three compounds due to the introduction of CH…N

hydrogen bonding which restricted the rotation between donor and acceptor and increased the structural rigidity[42]. Whereas, in MCZ-P2-DTM, the position of nitrogen was para to the donor group, and hence the molecule was more flexible than MCZ-P3-DTM; thus, it showed a lower PLQY than MCZ-P3-DTM.[42]

3.4. Electrochemical analysis

The electrochemical properties of these compounds were performed by cyclic voltammetry (CV). As depicted in **Figure 3**, all compounds displayed clear oxidation behaviors, which can be assigned to the oxidation of the MCZ moiety. Compared with MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM displayed lower reduction onset potentials, which can be assigned to the augment of electron-withdrawing capacity of the acceptor moieties induced by introduction of pyridine ring. The HOMO energy levels were calculated to be 5.38, 5.44 and 5.42 eV of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM, respectively, using the energy level of ferrocene (Fc) (4.8 eV) as a reference. The LUMO energy levels were estimated to be 2.42, 2.59 and 2.50 eV for MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM, respectively, which were calculated from the HOMOs and E_g.



Figure 3. Cyclic voltammograms of MCZ-B-DTM, MCZ-P2-DTM and MCZ-P2-DTM.

3.5. Theoretical calculations

The ground-state geometries and the frontier molecular orbital cloud distributions of these compounds were calculated using density functional theory (DFT) at the B3LYP/6-31G(d) level to better understand the influence of hydrogen bonding for the structures and electronic properties. The geometrical structures and calculated electron cloud distributions were displayed in **Figure 4**. The torsions between the donor and acceptor units were different among these three compounds. The dihedral angles between donor and acceptor were both 50° of MCZ-B-DTM and MCZ-P2-DTM, respectively, while the angle of MCZ-P3-DTM changed to 32°. This observed difference can be explained when considering the nitrogen atom in the pyridine ring and therefore the proximal C-H of MCZ locked the rotation between the MCZ and pyridine hybrid acceptor. In addition, the CH…N non-bonding distance was calculated to be 2.4 Å in MCZ-P3-DTM, revealing the strong CH…N bonding existed

between the pyridine and MCZ[6, 9]. Besides, the bond length of C-N (between the MCZ and pyridine or benzene rings) was 1.402 Å in MCZ-P3-DTM, which was short than 1.414 and 1.410 Å of MCZ-B-DTM and MCZ-P2-DTM, respectively, demonstrated that MCZ was more strongly bond with pyridine ring in MCZ-P3-DTM. These results further confirmed the strong intramolecular CH…N bonding interaction between the donor and acceptor in MCZ-P3-DTM.

On the other hand, The HOMOs were located on the MCZ moieties due to its strong electron donating property. It was worth noting that the HOMOs electron cloud distributed on the carbazole units simultaneously extended to the substitutive methoxy benzene part on its 3,6-position, which was beneficial for improve quantum yield and structural stability[43, 44]. However, subtle difference of the LUMO distributions in three molecules can be observed due to the different components in acceptor units. The LUMOs of the three emitters were mainly distributed on the central carbonyl. Meanwhile, the electron cloud extended to the MCZ unit slightly in MCZ-P3-DTM. Therefore, compared with MCZ-B-DTM and MCZ-P2-DTM, the orbital overlap of HOMO and LUMO were increased in MCZ-P3-DTM, which was beneficial for increasing quantum yield through enhancing the radiative processes[45].



Figure 4. Optimized molecule structures and HOMO/LUMO distributions calculated by using B3LYP/6-31g(d) level.

3.6. Electroluminescent properties

To evaluate the electroluminescence (EL) performance of these materials as emitters, TADF OLEDs were fabricated with the following commonly used device structure: indium tin oxide (ITO)/TAPC (30 nm)/mCP: 10 wt% emitters (50 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm). TAPC and TmPyPB were applied as the hole transporting layer (HTL) and the electron transporting layer (ETL). mCP with a triplet of 2.9 eV which was higher than the TADF emitters served as a host to construct the emitting layer (EML). The energy diagram of the devices and electroluminescent (EL) characteristics were showed in Figure 5, and the electroluminescent data were summarized in Table 2. The HOMO levels of the emitters were shallow than TAPC (-5.5 eV), so it can served as effective hole trapping sites for holes[36]. The EL spectra of the devices employed the three emitters were similar to the PL spectra from the corresponding 10% emitter doped mCP thin films (Figure S4 (d)), which implied that the devices with proper matching of energy levels leading to complete energy transfer from the host to dopants. The device employed MCZ-B-DTM as emitter displayed blue emission with the maximum peak at 467 nm and Commission International de l'Eclairage coordinates at (0.15, 0.20). The MCZ-P2-DTM and MCZ-P3-DTM based devices displayed sky-blue emission with maximum peaks at 496 and 486 nm and Commission International de l'Eclairage coordinates were (0.22, 0.44) and (0.19, 0.33), respectively. The turn-on voltages of the devices showed similar value from 3.2 to 3.5 V. The maximum EQEs of the devices were 7.5 and 9.7% of MCZ-B-DTM, MCZ-P2-DTM, respectively, whereas the device employed MCZ-P3-DTM as dopant displayed a maximum EQE of 12.1%. The relative high EQE of MCZ-P3-DTM based device mainly due to the higher PLQY stemmed from the introduction of intramolecular CH…N interactions.



Figure 5. (a) Energy diagram of the materials used in the devices; (b) Normalized EL spectra; (c) Current density-voltage-luminance (J-V-L) curves; (d) EQE versus luminance curves.

Comound	λ _{em} ª [nm]	V _{on} ^b [V]	L _{max} [cd m ⁻²]	η _{ext} [%]	η _c [cd A ⁻¹]	η_p [lm W ⁻¹]	CIE ^c (x,y)	
MCZ-B-DTM	467	3.4	4101	7.5	14.4	11.3	(0.15,0.20)	
MCZ-P2-DTM	496	3.5	10380	9.7	23.3	16.3	(0.22,0.44)	
MCZ-P3-DTM	484	3.2	13350	12.1	26.6	18.6	(0.19,0.33)	

 Table 2. Electroluminescence characteristics of the devices.

^aThe maximum emission recorded at 5 V.

^bTurn-on voltage measured at 1 cd m⁻².

^cCommission International de l'Eclairage coordinates at 5 V.

4. Conclusion

In summary, three novel TADF emitters (MCZ-B-DTM, MCZ-P2-DTM and MCZ-P3-DTM) were designed and synthesized based on pyridine hybrid acceptors and a donor of MCZ. The nitrogen atoms in pyridine rings were varied relative to the donor units to establish a comparative study with the parent molecule MCZ-B-DTM.

The formation of intramolecular CH···N interactions between donor and acceptor improved the PLQY of MCZ-P3-DTM resulted from the increased molecular structural rigidity. The device adopted MCZ-P3-DTM as emitter exhibiting a maximum EQE and CE of 12.1% and 26.6 cd/A, respectively, which was higher than those of MCZ-B-DTM and MCZ-P2-DTM. These results manifested that the formation of intramolecular hydrogen interactions was a promised way for the design of efficient blue TADF emitters.

Conflicts of interest

There are no conflicts to declare.

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References

[1] Goushi K, Yoshida K, Sato K, Adachi C. Organic light-emitting diodes employing efficient reverse intersystem crossing for triplet-to-singlet state conversion. Nature Photonics. 2012;6(4):253-8.

[2] Lee SY, Yasuda T, Yang YS, Zhang Q, Adachi C. Luminous butterflies: efficient exciton harvesting by benzophenone derivatives for full-color delayed fluorescence OLEDs. Angewandte Chemie. 2014;53(25):6402-6.

[3] Nakanotani H, Higuchi T, Furukawa T, Masui K, Morimoto K, Numata M, et al. High-efficiency organic light-emitting diodes with fluorescent emitters. Nature communications. 2014;5:4016.

[4] Chen XL, Jia JH, Yu R, Liao JZ, Yang MX, Lu CZ. Combining Charge-Transfer Pathways to Achieve Unique Thermally Activated Delayed Fluorescence Emitters for High-Performance Solution-Processed, Non-doped Blue OLEDs. Angewandte Chemie. 2017.

[5] Xiang C, Fu X, Wei W, Liu R, Zhang Y, Balema V, et al. Efficiency Roll-Off in Blue Emitting Phosphorescent Organic Light Emitting Diodes with Carbazole Host Materials. Advanced Functional Materials. 2016;26(9):1463-9.

[6] Jürgensen N, Kretzschmar A, Höfle S, Freudenberg J, Bunz UHF, Hernandez-Sosa G. Sulfone-Based Deep Blue Thermally Activated Delayed Fluorescence Emitters: Solution-Processed Organic

Light-Emitting Diodes with High Efficiency and Brightness. Chemistry of Materials. 2017;29(21):9154-61.

[7] Zhang Q, Li J, Shizu K, Huang S, Hirata S, Miyazaki H, et al. Design of efficient thermally activated delayed fluorescence materials for pure blue organic light emitting diodes. Journal of the American Chemical Society. 2012;134(36):14706-9.

[8] Shao S, Ding J, Wang L, Jing X, Wang F. Highly efficient blue electrophosphorescent polymers with fluorinated poly(arylene ether phosphine oxide) as Backbone. Journal of the American Chemical Society. 2012;134(37):15189-92.

[9] Kim KH, Liao JL, Lee SW, Sim B, Moon CK, Lee GH, et al. Crystal Organic Light-Emitting Diodes with Perfectly Oriented Non-Doped Pt-Based Emitting Layer. Advanced materials. 2016;28(13):2526-32.

[10] Kong FK, Tang MC, Wong YC, Chan MY, Yam VW. Design Strategy for High-Performance Dendritic Carbazole-Containing Alkynylplatinum(II) Complexes and Their Application in Solution-Processable Organic Light-Emitting Devices. Journal of the American Chemical Society. 2016;138(19):6281-91.

[11] Im Y, Kim M, Cho YJ, Seo J-A, Yook KS, Lee JY. Molecular Design Strategy of Organic Thermally Activated Delayed Fluorescence Emitters. Chemistry of Materials. 2017;29(5):1946-63.

[12] Cai X, Chen D, Gao K, Gan L, Yin Q, Qiao Z, et al. "Trade-Off" Hidden in Condensed State Solvation: Multiradiative Channels Design for Highly Efficient Solution-Processed Purely Organic Electroluminescence at High Brightness. Advanced Functional Materials. 2017:1704927.

[13] Albrecht K, Matsuoka K, Yokoyama D, Sakai Y, Nakayama A, Fujita K, et al. Thermally activated delayed fluorescence OLEDs with fully solution processed organic layers exhibiting nearly 10% external quantum efficiency. Chemical communications. 2017;53(16):2439-42.

[14] Zeng W, Lai HY, Lee WK, Jiao M, Shiu YJ, Zhong C, et al. Achieving Nearly 30% External Quantum Efficiency for Orange-Red Organic Light Emitting Diodes by Employing Thermally Activated Delayed Fluorescence Emitters Composed of 1,8-Naphthalimide-Acridine Hybrids. Advanced materials. 2017.

[15] Park HJ, Han SH, Lee JY. Molecular Design of Thermally Activated Delayed-Fluorescent Emitters
 Using 2,2'-Bipyrimidine as the Acceptor in Donor-Acceptor Structures. Chemistry, an Asian journal.
 2017;12(18):2494-500.

[16] Zhao H, Wang Z, Cai X, Liu K, He Z, Liu X, et al. Highly efficient thermally activated delayed fluorescence materials with reduced efficiency roll-off and low on-set voltages. Mater Chem Front. 2017;1(10):2039-46.

[17] Park H-J, Han SH, Lee JY. A directly coupled dual emitting core based molecular design of thermally activated delayed fluorescent emitters. Journal of Materials Chemistry C. 2017.

[18] Okazaki M, Takeda Y, Data P, Pander P, Higginbotham H, Monkman AP, et al. Thermally activated delayed fluorescent phenothiazine-dibenzo[a,j]phenazine-phenothiazine triads exhibiting tricolor-changing mechanochromic luminescence. Chemical science. 2017;8(4):2677-86.

[19] Guo J, Zhao Z, Tang BZ. Purely Organic Materials with Aggregation-Induced Delayed Fluorescence for Efficient Nondoped OLEDs. Advanced Optical Materials. 2018:1800264.

[20] Liu M, Seino Y, Chen D, Inomata S, Su SJ, Sasabe H, et al. Blue thermally activated delayed fluorescence materials based on bis(phenylsulfonyl)benzene derivatives. Chemical communications. 2015;51(91):16353-6.

[21] Kim M, Jeon SK, Hwang SH, Lee SS, Yu E, Lee JY. Highly efficient and color tunable thermally activated delayed fluorescent emitters using a "twin emitter" molecular design. Chemical communications. 2016;52(2):339-42.

[22] Furue R, Matsuo K, Ashikari Y, Ooka H, Amanokura N, Yasuda T. Highly Efficient Red-Orange

Delayed Fluorescence Emitters Based on Strong π -Accepting Dibenzophenazine and Dibenzoquinoxaline Cores: toward a Rational Pure-Red OLED Design. Advanced Optical Materials. 2018:1701147.

[23] Wada Y, Kubo S, Kaji H. Adamantyl Substitution Strategy for Realizing Solution-Processable Thermally Stable Deep-Blue Thermally Activated Delayed Fluorescence Materials. Advanced materials. 2018.

[24] Kim KJ, Kim GH, Lampande R, Ahn DH, Im JB, Moon JS, et al. A new rigid diindolocarbazole donor moiety for high quantum efficiency thermally activated delayed fluorescence emitter. Journal of Materials Chemistry C. 2018.

[25] Chan C-Y, Cui L-S, Kim JU, Nakanotani H, Adachi C. Rational Molecular Design for Deep-Blue Thermally Activated Delayed Fluorescence Emitters. Advanced Functional Materials. 2018:1706023.

[26] Yu L, Wu Z, Xie G, Zhong C, Zhu Z, Ma D, et al. An efficient exciton harvest route for high-performance OLEDs based on aggregation-induced delayed fluorescence. Chemical communications. 2018;54(11):1379-82.

[27] Wei D, Ni F, Wu Z, Zhu Z, Zou Y, Zheng K, et al. Designing dual emitting cores for highly efficient thermally activated delayed fluorescent emitters. Journal of Materials Chemistry C. 2018;6(43):11615-21.

[28] Cho YJ, Jeon SK, Chin BD, Yu E, Lee JY. The design of dual emitting cores for green thermally activated delayed fluorescent materials. Angewandte Chemie. 2015;54(17):5201-4.

[29] Cui LS, Nomura H, Geng Y, Kim JU, Nakanotani H, Adachi C. Controlling Singlet-Triplet Energy Splitting for Deep-Blue Thermally Activated Delayed Fluorescence Emitters. Angewandte Chemie. 2017;56(6):1571-5.

[30] Komatsu R, Ohsawa T, Sasabe H, Nakao K, Hayasaka Y, Kido J. Manipulating the Electronic Excited State Energies of Pyrimidine-Based Thermally Activated Delayed Fluorescence Emitters To Realize Efficient Deep-Blue Emission. ACS applied materials & interfaces. 2017;9(5):4742-9.

[31] Huang W, Einzinger M, Zhu T, Chae HS, Jeon S, Ihn S-G, et al. Molecular Design of Deep Blue Thermally Activated Delayed Fluorescence Materials Employing a Homoconjugative Triptycene Scaffold and Dihedral Angle Tuning. Chemistry of Materials. 2018;30(5):1462-6.

[32] Lee DR, Choi JM, Lee CW, Lee JY. Ideal Molecular Design of Blue Thermally Activated Delayed Fluorescent Emitter for High Efficiency, Small Singlet–Triplet Energy Splitting, Low Efficiency Roll-Off, and Long Lifetime. ACS applied materials & interfaces. 2016;8(35):23190-6.

[33] Lee YH, Park S, Oh J, Shin JW, Jung J, Yoo S, et al. Rigidity-Induced Delayed Fluorescence by Ortho Donor-Appended Triarylboron Compounds: Record-High Efficiency in Pure Blue Fluorescent Organic Light-Emitting Diodes. ACS applied materials & interfaces. 2017;9(28):24035-42.

[34] Chen DY, Liu W, Zheng CJ, Wang K, Li F, Tao SL, et al. Isomeric Thermally Activated Delayed Fluorescence Emitters for Color Purity-Improved Emission in Organic Light-Emitting Devices. ACS applied materials & interfaces. 2016;8(26):16791-8.

[35] Ganesan P, Chen D-G, Liao J-L, Li W-C, Lai Y-N, Luo D, et al. Isomeric spiro-[acridine-9,9'

-fluorene]-2,6-dipyridylpyrimidine based TADF emitters: insights into photophysical behaviors and OLED performances. Journal of Materials Chemistry C. 2018;6(37):10088-100.

[36] Park H-J, Han SH, Lee JY, Han H, Kim E-G. Managing Orientation of Nitrogens in Bipyrimidine-Based Thermally Activated Delayed Fluorescent Emitters To Suppress Nonradiative Mechanisms. Chemistry of Materials. 2018;30(10):3215-22.

[37] Chen X-K, Tsuchiya Y, Ishikawa Y, Zhong C, Adachi C, Brédas J-L. A New Design Strategy for Efficient

Thermally Activated Delayed Fluorescence Organic Emitters: From Twisted to Planar Structures. Advanced materials. 2017;29(46):1702767.

[38] Bahamonde A, Murphy JJ, Savarese M, Bremond E, Cavalli A, Melchiorre P. Studies on the Enantioselective Iminium Ion Trapping of Radicals Triggered by an Electron-Relay Mechanism. Journal of the American Chemical Society. 2017;139(12):4559-67.

[39] Guo J, Li X-L, Nie H, Luo W, Gan S, Hu S, et al. Achieving High-Performance Nondoped OLEDs with Extremely Small Efficiency Roll-Off by Combining Aggregation-Induced Emission and Thermally Activated Delayed Fluorescence. Advanced Functional Materials. 2017;27(13):1606458.

[40] Chen Z-P, Wang D-Q, Zhang M, Wang K, Shi Y-Z, Chen J-X, et al. Optimization on Molecular Restriction for Highly Efficient Thermally Activated Delayed Fluorescence Emitters. Advanced Optical Materials. 2018;6(24):1800935.

[41] Li X, Wang K, Shi Y-Z, Zhang M, Dai G-L, Liu W, et al. Efficient solution-processed orange-red organic light-emitting diodes based on a novel thermally activated delayed fluorescence emitter. Journal of Materials Chemistry C. 2018;6(34):9152-7.

[42] Rajamalli P, Senthilkumar N, Huang PY, Ren-Wu CC, Lin HW, Cheng CH. New Molecular Design Concurrently Providing Superior Pure Blue, Thermally Activated Delayed Fluorescence and Optical Out-Coupling Efficiencies. Journal of the American Chemical Society. 2017;139(32):10948-51.

[43] Rajamalli P, Thangaraji V, Senthilkumar N, Ren-Wu C-C, Lin H-W, Cheng C-H. Thermally activated delayed fluorescence emitters with a m,m-di-tert-butyl-carbazolyl benzoylpyridine core achieving extremely high blue electroluminescence efficiencies. Journal of Materials Chemistry C. 2017;5(11):2919-26.

[44] Rajamalli P, Senthilkumar N, Gandeepan P, Ren-Wu CC, Lin HW, Cheng CH. A Method for Reducing the Singlet-Triplet Energy Gaps of TADF Materials for Improving the Blue OLED Efficiency. ACS applied materials & interfaces. 2016;8(40):27026-34.

[45] Wong W-YR, Zhang Y, Chen Z, Song J, He J, Wang X, et al. Rational design of high efficiency green to deep red/near-infrared emitting materials based on isomeric donor-acceptor chromophores. Journal of Materials Chemistry C. 2018.

- Higher absorption coefficient achieved by introducing hydrogen bonding into the molecule.
- Formation of intramolecular CH…N hydrogen bonding between donor and acceptor enhances the molecule rigidity with increased PLQY and EQE.
- Comparative study is carried out by varied the position of nitrogen atom in pyridine.
- This strategy is promising to achieve high efficient blue TADF emitters.