Planar and Rigid Pyrazine-Based TADF Emitter for Deep Blue Bright Organic Light-Emitting Diodes

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Two blue thermally activated delayed fluorescence (TADF) emitters bearing di-*tert*-butyl carbazoles as the electron donor groups and pyrazine (DTCz-Pz) or dipyrazine (DTCz-DPz) as the electron acceptor are presented. The DFT calculations predict DTCz-Pz and DTCz-DPz to possess high S_1 energies (3.19 eV and 3.08 eV, respectively), and relatively large ΔE_{ST} values (0.52 eV and 0.56 eV, respectively). The closely layered intermediate triplet states between S_1 and T_1 , predicted by DFT calculations, are expected to facilitate the reverse intersystem crossing (RISC) and improve spin-vibronic coupling efficiency between the excited states, even the relatively larger ΔE_{ST} s. The

ΔE_{ST} s for DTCz-Pz and DTCz-DPz are 0.27 eV and 0.38 eV, and both molecules show high photoluminescence quantum yields (65 %, and 70 %, respectively). The decay lifetimes show temperature dependence in a PPT host, which is consistent with the fact that both molecules are TADF emitters in PPT. The OLEDs based on DTCz-Pz exhibit deep blue emission with λ_{EL} of 460 nm and CIE of (0.15, 0.16). The maximum external quantum efficiency (EQE_{max}) reaches 11.6 %, with a maximum luminance (L_{max}) of up to 6892 $cd\ m^{-2}$, while the device based on DTCz-DPz exhibits sky blue emission with λ_{EL} of 484 nm and CIE of (0.15, 0.30), an EQE_{max} of 7.2 %, and L_{max} of 8802 $cd\ m^{-2}$.

Introduction

Recently, organic light-emitting diodes (OLEDs) using organic thermally activated delayed fluorescence (TADF) emitters have generated great interest as a cheaper alternative to phosphorescent OLEDs based on noble metal complexes.^[1–3] Triplet excitons can be converted to singlet excitons in TADF materials via reverse intersystem crossing (RISC) due to the presence of a very small singlet-triplet energy gap (ΔE_{ST}). This was realized by a molecular design that localizes the HOMO on a donor moiety and the LUMO on an acceptor moiety, usually incorporated within a highly twisted structure. Although a plethora of TADF emitters has been developed since the first examples of high-efficiency TADF OLEDs in 2012,^[1] deep blue TADF OLEDs (CIE coordinates where $x < 0.15$, $y < 0.20$) remain underdeveloped, and their efficiencies and stabilities are still generally lower than sky blue and green TADF OLEDs.^[4,5] Therefore, the development

of alternative, highly efficient blue-emitting materials remains highly desired. Sensible molecular structure design as well as electron donor and acceptor selection are required in order to obtain deep blue emission.

The nitrogen-containing heterocyclic acceptor triazine has been used widely in blue TADF emitters due to its high triplet energy (3.27 eV in 3-methylpentane^[6]) and relatively weak electron-accepting properties ($E_{red}^{1/2} = -2.1$ V vs SCE in MeCN^[7]).^[8–10] A prototypical example, **DMAC-TRZ**, contains a 2,4,6-triphenyl-1,3,5-triazine (TRZ) as the electron-acceptor and 9,9-dimethyl-9,10-dihydroacridine (DMAC) as the electron donor. This compound is a sky-blue emitter where the OLED showed $\lambda_{EL} = 504$ nm and CIE coordinates of (0.22, 0.50) in mPCPN and, along with a high maximum external quantum efficiency (EQE_{max}) of 26.5 %. Researchers have tried to tune the emission color further towards the blue through structure optimization (Figure 1).^[11] Kaji *et al.* aimed decreasing the electron affinity of the electron acceptor by replacing the non-bridging phenyl rings in TRZ with adamantyl groups. The molecule **MA-TA** exhibited a destabilized LUMO of -2.96 eV compared to -3.12 eV for **DMAC-TRZ**, and a correspondingly destabilized S_1 level of 2.90 eV (in toluene) compared to 2.74 eV (in toluene) for **DMAC-TRZ**.^[9,11] As a result, the OLED using **MA-TA** exhibited deep-blue emission with $\lambda_{EL} = 465$ nm and CIE coordinates of (0.15, 0.16), along with a high EQE_{max} of 22.1 %.^[9] Adachi *et al.* further pushed the color towards the deep-blue region by using a weaker electron donor in 3,6-dimethylcarbazole coupled with a methylphenylene bridge that, due to the presence of the methyl group, increasing the torsion angle of the donor, leading to reduced conjugation, smaller ΔE_{ST} and a higher S_1 energy.^[8] The molecule **Cz-TRZ3** possesses a shallow LUMO of -2.71 eV (in DCM) and a high S_1 energy of 3.10 eV (in toluene).^[8] The OLEDs based on **Cz-TRZ3** exhibited deep-blue emission with CIE coordinates (0.15, 0.10) and EQE_{max}

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of 19.2%.^[8] On the other hand, Chou *et al.* found that by simply replacing the triazine with pyrimidine can push the emission to higher energy as well.^[12] The molecule **T3** possesses a much

destabilized LUMO energy of -2.37 eV (in MeCN) and an S_1 energy of 2.95 eV (in toluene), while the device based on **T3** exhibited blue emission with $\lambda_{\text{EL}} = 465$ nm and CIE coordinates

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Recent awards he has received include a 2019 the 24th Nagoya of Organic Chemistry "the silver medal", a 2017 Nishina Memorial Prize and a 2016 Thomson Reuters Research Front Award, and he was named a 2018–2019 Highly Cited Researcher for the Cross-Field category.

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Figure 1. Chemical structures of heteroaromatic acceptor in blue TADF emitters design.

of (0.17, 0.21) and an EQE_{max} of 11.8%.^[12] Wang *et al.* further blue-shifted the emission by using bespoke acridine-carbazole fused donor, and the bulky donor makes the molecule **12AcCz-PM** adopt a quasi-orthogonal conformation.^[13] The S_1 of **12AcCz-PM** is 3.06 eV while the LUMO value is similar to **T3** at -2.31 eV (in MeCN).^[13] The OLEDs based on **12AcCz-PM** exhibited deep blue emission with $\lambda_{\text{EL}} = 438$ nm and CIE coordinates (0.15, 0.06); however, the EQE_{max} was only 5.7% due in part to the large ΔE_{ST} (0.39 eV in DPEPO).^[13]

These examples in the literature have shown that triazine and pyrimidine acceptors are compatible with obtaining blue and deep blue TADF emitters and reasonably high efficiencies in OLEDs. The related N-heterocycle, pyrazine, has thus far not been explored for blue TADF emitter design, though the pyrazine has been used within an electron-acceptor design to tune its electron affinity and the corresponding energies of the emitters.^[14–16] Recently, Duan *et al.* reported a series of blue TADF emitters bearing pyrazine as an acceptor and benzofuro-carbazoles or benzothieno-carbazoles as donor moieties.^[17] Amongst the molecules in the study, **BFCZPZ2** possessed a moderately small ΔE_{ST} (0.31 eV in PPT) and high photoluminescence quantum yield (PLQY) (91% in PPT).^[17] The device based on **BFCZPZ2** exhibited deep blue emission with $\lambda_{\text{EL}} = 464$ nm and CIE coordinates of (0.15, 0.16), and the EQE_{max} reached 21.3%, but reduced to 5.1% at 10 mA/cm².^[17] This work showed the potential of pyrazine in the design of blue TADF materials.

In this work, we report two TADF emitters, 2,5-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)pyrazine (**DTCz-Pz**) and 5,5'-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)-2,2'-bipyrazine (**DTCz-DPz**) (Figure 1). Both **DTCz-Pz** and **DTCz-DPz** possess a planar geometry showing high PLQY, Φ_{PL} in doped thin films (70% and 65% in PPT, respectively). Although the ΔE_{ST} s of **DTCz-Pz** and **DTCz-DPz** are relatively large (0.27 eV and 0.38 eV in PPT, respec-

tively), the presence of an intermediate triplet state provides a viable route for TADF. The OLEDs based on **DTCz-Pz** and **DTCz-DPz** exhibit deep blue and sky-blue emission with CIE coordinates of (0.15, 0.16) and (0.15, 0.30), and maximum EQE of 11.6% and 7.2%, respectively.

Results and Discussion

Theoretical Calculations

The ground state (S_0) geometries of **DTCz-Pz** and **DTCz-DPz** were optimized by Density functional theory (DFT) and the excited states and their electronic configuration were predicted by time-dependent DFT calculations using the Tamm-Dancoff approximation (TDA-DFT) at the PBE0/6-31G(d,p) level of theory in the gas phase.^[18,19] The results are summarized in Figure 2. The DFT modeling predicts a rather flat conformation with average dihedral angles between the DTCz moieties and the pyrazine ring(s) of [36.53(14)°] and [32.70(4)°], for **DTCz-Pz** and **DTCz-DPz**, respectively. The relatively small dihedral angles align with those observed in the single crystal for a related TADF emitter, **DTCz-DPzS** [38.20(8)°], where the pyrazine ring was similarly connected to carbazole, indicating a likely intramolecular hydrogen bonding, analogously to that observed by us for related dipyrazinylsulfone TADF emitters.^[14] In both emitters, the HOMOs are distributed across the entire molecule while the LUMOs are mainly localized on the acceptor cores. The more strongly electron-accepting DPz in **DTCz-DPz** results in more stabilized HOMO and LUMO levels compared to those in **DTCz-Pz**. Analogously, the S_1 and T_1 levels are predicted to be slightly stabilized in **DTCz-DPz** compared to **DTCz-Pz**. Both

Figure 2. Theoretical modelling of the energies of the HOMO/LUMO orbitals and the S_1 and T_1 states of DTCz-Pz and DTCz-DPz in the gas phase and the electron density distribution of the frontier molecular orbitals (isovalue = 0.02).

emitters show high oscillator strength (0.24 and 1.39 for DTCz-Pz and DTCz-DPz, respectively) and large ΔE_{ST} values (0.52 eV for DTCz-Pz and 0.56 eV for DTCz-DPz). The higher energy intermediate triplet states of DTCz-Pz and DTCz-DPz were also studied (Figure S9). For DTCz-Pz, the T_2 state (3.18 eV) is nearly degenerate with the S_1 state (3.19 eV). For DTCz-DPz, the T_2 state at 2.85 eV results in a $\Delta E_{S_{1T_2}}$ of 0.23 eV. The nature of the T_2 states for DTCz-Pz and DTCz-DPz is of locally excited (LE) character [HOMO to LUMO + 1 (85%) for DTCz-Pz, HOMO-1 to LUMO + 1 (40%) for DTCz-DPz] distributed over the whole molecule. This is different from the S_1 and T_1 states, which are dominated by a hybrid CT and LE transition from HOMO to LUMO. The presence of an intermediate T_2 state that is of different symmetry to S_1 in both DTCz-Pz and DTCz-DPz will contribute to a more efficient TADF as RISC will be faster, facilitated by spin-vibronic coupling between T_1 and T_2 and enhanced spin-orbit coupling (SOC) between T_2 and S_1 .^[20,21] We calculated the $|V_{SOC}|^2$ values as the average spin-orbital coupling matrix elements (SOCME) between their S_1/T_1 states and S_1/T_2 states based on their optimized excited-state structures,^[22] which are shown in Table 1. The $|V_{SOC}|^2$ value between S_1/T_1 for DTCz-Pz is 0.017 cm⁻² and this increases to 0.517 cm⁻² for S_1/T_2 due to the different orbital character of T_2 compared to S_1 . Analogously, the $|V_{SOC}|^2$ values for DTCz-DPz also increases from 0.003 cm⁻² (between S_1/T_1) to 0.170 cm⁻² (between S_1/T_2). The closely layered intermediate T_2 state and high SOCME values between the S_1/T_2 states provide an indirect route for RISC to occur despite the relatively large ΔE_{ST} for DTCz-Pz and DTCz-DPz.

Synthesis

DTCz-Pz was obtained in 77% yield via an Ullmann coupling reaction between two equivalents of 3,6-di-*tert*-butyl-9H-carbazole (DTCz) and 2,5-dibromopyrazine. DTCz-DPz was obtained in moderate yield in a two-step protocol involving an Ullmann coupling between DTCz and 2-bromo-5-iodopyrazine followed by homocoupling of intermediate DTCzPzBr catalyzed by Pd(PPh₃)₄ (Scheme 1). Both emitters were characterized by combination of ¹H and ¹³C NMR spectroscopy (Figures S1–S4), high-resolution mass spectrometry, melting point determination, and elemental analysis (Figures S5–S6). The two emitters were purified by silica gel chromatography followed by temperature gradient vacuum sublimation, and the purity was verified by high performance liquid chromatography (HPLC) analysis (Figures S7–S8). The thermal properties of these emitters were determined by thermogravimetric analysis (Figure S13). The results show that these compounds possess very high T_d (5% weight loss) of 411 °C and 459 °C, respectively for DTCz-Pz and DTCz-DPz.

Electrochemistry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements of DTCz-Pz and DTCz-DPz were carried out in dichloromethane (DCM) to estimate the HOMO and LUMO energies (Figure 3a). The CV trace of DTCz-Pz shows a pseudo-reversible oxidation wave with E_{ox} = 1.22 V (obtained

Table 1. Excited states energies, ΔE_{ST} s, and average $|V_{SOC}|^2$ values of DTCz-Pz and DTCz-DPz.^[a]

Compound	S_1 [eV]	T_1 [eV]	ΔE_{ST} [eV]	$ V_{SOC}^{S_1/T_1} ^2$ [cm ⁻²]	T_2 [eV]	$\Delta E_{S_{1T_2}}$ [eV]	$ V_{SOC}^{S_1/T_2} ^2$ [cm ⁻²]
DTCz-Pz	3.19	2.67	0.52	0.017	3.18	0.01	0.517
DTCz-DPz	3.08	2.52	0.56	0.003	2.85	0.23	0.170

[a] S_1 = singlet state energy; T_1 = triplet state; $\Delta E_{ST} = E(S_1) - E(T_1)$; $|V_{SOC}^{S_1/T_1}|^2$: SOCME between S_1 and T_1 ; $|V_{SOC}^{S_1/T_2}|^2$: SOCME between S_1 and T_2 .

Scheme 1. Synthesis route of DTCz-Pz and DTCz-DPz.

Figure 3. a) Cyclic Voltammograms (CV, solid lines) and Differential Pulse Voltammograms (DPV, dashed lines) for DTCz-Pz and DTCz-DPz in degassed DCM solution containing $[n\text{Bu}_4\text{N}]\text{PF}_6$ as the supporting electrolyte and using Fc/Fc^+ as an external standard ($\text{Fc}/\text{Fc}^+ = 0.46$ eV versus $\text{SCE}^{[23]}$, scan rate = 100 mVs $^{-1}$). b) Photoemission yield spectra of DTCz-Pz and DTCz-DPz.

from DPV) while DTCz-DPz exhibited an irreversible oxidation with $E_{\text{ox}} = 1.23$ V (obtained from DPV). No reduction wave was observed for either compound within the DCM solvent window. The corresponding HOMO levels of DTCz-Pz and DTCz-DPz are -5.56 eV and -5.57 eV. Photoemission yield spectroscopy in air was used to measure the HOMO levels of neat thin films of the two emitters (Figure 3b) with values of -5.87 eV and -5.98 eV for DTCz-Pz and DTCz-DPz, respectively, which also qualitatively match the trends obtained from the DFT calculations and the electrochemistry. The LUMO levels for DTCz-Pz (-2.58 eV), and DTCz-DPz (-2.73 eV) were inferred from the HOMO energies and the optical gap (E_g), which itself was determined from the intersection of the normalized absorption and fluorescence spectra in toluene (2.98 and 2.84 eV, respectively, for DTCz-Pz and DTCz-DPz, Figure S14).

Photophysical properties

The UV-vis absorption spectra of both emitters in toluene are shown in Figure 4a. The profiles match closely to the calculated absorption spectra by TDA-DFT (Figure S10). The TDA-DFT calculations predict that both emitters should exhibit hybridized

local and charge-transfer (HLCT) transitions from HOMO to LUMO at 380 nm for DTCz-Pz and 400 nm for DTCz-DPz. For DTCz-DPz, the molar absorptivity of this band is much higher than that of DTCz-Pz due to the larger HOMO/LUMO overlap, which aligns with the predicted high oscillator strength. The absorption bands at 330 nm and 300 nm for DTCz-Pz are assigned to locally excited (LE) $\pi \rightarrow \pi^*$ transitions on the whole molecule and carbazole moiety, respectively, by TDA-DFT calculation (Table S2). For DTCz-DPz, TDA-DFT predicted a higher energy HLCT transition on 340 nm and a LE transition on the carbazole moiety at 300 nm (Table S3). The oscillator strengths (f) for DTCz-Pz and DTCz-DPz are calculated to be 0.2514 and 0.5255, respectively, from the spectra, $^{[24]}$ which are consistent with the trend observed from the TDADFT calculations (0.2414 and 1.3927, respectively). The steady-state PL spectra for DTCz-Pz and DTC-DPz are shown in Figure 4b and Figure 4c, respectively. In toluene, DTCz-Pz shows structureless emission with λ_{PL} of 441 nm, suggesting emission from a CT state, while the profile for DTCz-DPz in toluene has a slightly red-shifted λ_{PL} of 455 nm. In *n*-hexane, both compounds show structured emission, though this is more pronounced in DTCz-DPz, indicating emission from an LE state. There is a modest positive solvatochromism observed for DTCz-Pz while the

Figure 4. a) Absorption spectra of **DTCz-Pz** and **DTCz-DPz** in toluene; b) Solvatochromic PL study of **DTCz-Pz**; c) Solvatochromic PL study of **DTCz-DPz** ($\lambda_{\text{exc}} = 360$ nm).

positive solvatochromism is more significant in **DTCz-DPz**, suggesting a more pronounced CT emissive state in this compound.

The time-resolved PL decays of these materials were measured in 10^{-5} M toluene solution under nitrogen (Figure 5). In both compounds, the emission decays with bi-exponential kinetics. There is a nanosecond prompt emission, which occurs

Figure 5. Transient PL decay of a) **DTCz-Pz** and b) **DTCz-DPz** in toluene ($\lambda_{\text{exc}} = 378$ nm).

from direct radiative depopulation of the S_1 state with τ_1 of 6.0 ns (63.4%) and 2.9 ns (85.7%) for **DTCz-Pz** and **DTCz-DPz**, respectively. There is a second component with a lifetime (τ_2) of 93 ns (36.6%) and 121 ns (14.3%) for **DTCz-Pz** and **DTCz-DPz**, respectively. Delayed emission is not observed for these compounds in solution.

We next investigated the photophysical properties of the two emitters in a high triplet energy host matrix, PPT ($E_T = 2.95$ eV) and the photophysical properties are summarized in Table 2.^[25] Thin films of each emitter doped at 7 wt% in PPT were prepared by vacuum deposition. **DTCz-Pz** shows structureless, broad emission for both prompt fluorescence and phosphorescence at 77 K, pointing to ^1CT and ^3CT states (Figure 6). By contrast, **DTCz-DPz** shows broad emission for the prompt fluorescence spectrum and structured emission for the phosphorescence spectrum, indicating that for the latter, emission originates from a LE state on the DPz moiety. The calculated ΔE_{ST} values determined from the onsets of the prompt fluorescence and phosphorescence spectra are 0.27 eV and 0.38 eV for **DTCz-Pz** and **DTCz-DPz**, respectively.

The temperature-dependent time-resolved PL decays in doped PPT films are shown in Figure 7. The relative intensities of the delayed PL of both **DTCz-Pz** and **DTCz-DPz** decreased with decreasing temperature, which is the typical behavior for TADF emitters. Both compounds show a dominant prompt nanosecond fluorescence component and only a very small

Table 2. Photophysical properties of DTCz-Pz and DTCz-DPz in PPT. ^[a]						
Compound	S_1 [eV]	T_1 [eV]	ΔE_{ST} [eV]	Φ_{PL} [%]	τ_p [ns]	τ_d [ms]
DTCz-Pz	2.93	2.66	0.27	58 (air), 70 (N_2)	7.2 (77.7%) 10.7 (22.3%)	0.2 (4.9%) 1.7 (26.5%) 7.3 (68.6%)
DTCz-DPz	2.80	2.42	0.38	60 (air), 65 (N_2)	1.3 (16.9%) 3.4 (71.7%) 7.6 (11.3%)	0.1 (16.5%) 1.9 (35.8%) 15.4 (47.7%)

[a] S_1 = singlet state energy obtained from the onset of the prompt fluorescence spectra (1–100 ns) measured at 77 K with $\lambda_{\text{exc}} = 343$ nm; T_1 = triplet state energy obtained from the onset of the phosphorescence spectra (1–10 ms) measured at 77 K with $\lambda_{\text{exc}} = 343$ nm; $\Delta E_{\text{ST}} = E(S_1) - E(T_1)$; Φ_{PL} = photoluminescence quantum yield measured using an integrating sphere under nitrogen flow with $\lambda_{\text{exc}} = 340$ nm; τ_p = prompt fluorescence lifetime measured at room temperature with time window of 100 ns ($\lambda_{\text{exc}} = 378$ nm). τ_d = delayed fluorescence lifetime measured at room temperature with time window of 1–40 ms ($\lambda_{\text{exc}} = 378$ nm). All measurements were performed in co-doped PPT film (7 wt%).

Figure 6. Prompt fluorescence (FI, 1–100 ns) and phosphorescence (Phos., 1–10 ms) spectra of a) **DTCz-Pz** and b) **DTCz-DPz** at 77 K as 7 wt% doped PPT films ($\lambda_{\text{exc}} = 343$ nm).

Figure 7. Normalized temperature-dependent transient PL decays of a) **DTCz-Pz** and b) **DTCz-DPz** in 7 wt% doped PPT films ($\lambda_{\text{exc}} = 378$ nm).

Table 3. Electroluminescence performances of **DTCz-Pz** and **DTCz-DPz**.

Device	EQE [%]	L_{max} [cd/m^2]	CE_{max} [cd A^{-1}]	PE_{max} [lm W^{-1}]	CIE (@ 8 V) (λ_{EL} [nm])
DTCz-Pz	11.6 ^[a] /4.5 ^[b] /2.5 ^[c]	6892	13	11	0.15, 0.16 (460)
DTCz-DPz	7.2 ^[a] /3.8 ^[b] /2.8 ^[c]	8802	14	11	0.15, 0.30 (484)

[a] Maximum EQE. [b] EQE at $100 \text{ cd}/\text{m}^2$. [c] EQE at $1000 \text{ cd}/\text{m}^2$. L_{max} , maximum luminance; CE, current efficiency; PE, power efficiency; λ_{EL} , the wavelength where the EL spectrum has the highest intensity.

delayed microsecond fluorescence component. For **DTCz-Pz**, the prompt fluorescence decays with bi-exponential kinetics with lifetimes of 7.2 ns (77.7%) and 10.7 ns (22.3%), while the delayed fluorescence decays according to triexponential kinetics with lifetimes of 0.2 ms (4.9%), 1.7 ms (26.5%), 7.3 ms (68.6%). For **DTCz-DPz**, the prompt fluorescence lifetimes are 1.3 ns (16.9%), 3.4 ns (71.7%), 7.6 ns (11.3%) and the delayed fluorescence lifetimes are 0.1 ms (16.5%), 1.9 ms (35.8%), and 15.4 ms (47.7%). The significantly longer delayed lifetimes in

DTCz-DPz are consistent with the larger ΔE_{ST} value. The delayed lifetimes are significantly reduced under air with τ_d of 4.2 μs (99.1%) for **DTCz-Pz** and 4.0 μs (99.5%) for **DTCz-DPz** (Figure 8).

The absolute Φ_{PL} values measured using an integrating sphere under argon and air for the toluene solutions, and co-doped films are summarized in Table 2. **DTCz-DPz** shows significantly higher Φ_{PL} of 96% in degassed toluene than **DTCz-Pz** (69%), while the 7 wt% PPT doped films are similarly bright with Φ_{PL} of 70% and 65% for **DTCz-Pz** and **DTCz-DPz**, respectively.

Figure 8. Transient PL decays of a) **DTCz-Pz** and b) **DTCz-DPz** co-doped at 7 wt% in PPT film, measured under vacuum and air ($\lambda_{\text{exc}} = 378$ nm).

Figure 9. a) Luminance vs EQE, b) EL spectra of device (Inset: Photograph of device **DTCz-Pz** and **DTCz-DPz**), c) Current density-voltage-luminance characteristics, and d) Device structure: ITO/TAPC (40 nm)/mCP (10 nm)/PPT: **DTCz-Pz** or **DTCz-DPz** (7 wt%) (30 nm)/PPT (10 nm)/TmPyPB (30 nm)/LiF (0.7 nm)/Al (100 nm).

OLEDs

Next, we investigated the electroluminescence (EL) properties of these two emitters. Multilayer devices were fabricated using these materials as dopants with the following structures: ITO/

TAPC (40 nm)/mCP (10 nm)/PPT: **DTCz-Pz** or **DTCz-DPz** (7 wt%) (30 nm)/PPT (10 nm)/TmPyPB (30 nm)/LiF (0.7 nm)/Al (100 nm). The performance of the devices is summarized in Figure 8 and Table 3. EQE-luminance curves reveal a maximum EQE (EQE_{max}) of 11.6% for the **DTCz-Pz** device and 7.2% for the **DTCz-DPz**

device (Figure 9a). These devices show significant efficiency roll-off at high luminance. DTCz-Pz and DTCz-DPz-based devices show EQE₁₀₀ of 4.5% and 3.8% at 100 cd/m² and EQE₁₀₀₀ is further reduced to 2.5%, 2.8% at 1000 cd/m², respectively. The EL spectra show the deep blue (for the DTCz-Pz device) and sky blue (for the DTCz-DPz device) emission with CIE coordinates of (0.15, 0.16) and (0.15, 0.30), respectively. High maximum luminance values of 6892 cd/m² and 8802 cd/m² were obtained for DTCz-Pz and DTCz-DPz devices, respectively.

Conclusions

We have synthesized two pyrazine-based emitters DTCz-Pz and DTCz-DPz bearing a mono and dipyrazine acceptors and di-*tert*-butyl carbazole as the donor group. These two materials show reasonably high photoluminescence quantum yields, ranging from 76 to 96%, in both toluene solution and doped PPT thin films. The transient PL decay results in the doped thin film confirm that these compounds are TADF emitters. Blue-emitting OLEDs were fabricated using these emitting materials. The devices showed EQE_{max} of 11.6% for the DTCz-Pz device with CIE (0.15, 0.16) and 7.2% for the DTCz-DPz device with CIE (0.15, 0.30).

Supporting Information

A previous version of this manuscript has been deposited on a preprint server (DOI: doi.org/10.26434/chemrxiv.13626668.v1). Instrumentation details, synthesis and chemical characterization (NMR spectra, elemental analysis reports, HPLC chromatograms), computational details are available in supporting information. The research data supporting this publication can be accessed at <https://doi.org/10.17630/3008d05b-2053-435f-80a8-91f7b544bf51>.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Delayed fluorescence · Donor-acceptor · Organic light-emitting diodes · Pyrazine · TADF

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FULL PAPERS

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Planar and Rigid Pyrazine-Based TADF Emitter for Deep Blue Bright Organic Light-Emitting Diodes

Two blue donor-acceptor thermally activated delayed fluorescence (TADF) emitters containing pyrazine or dipyr-
azine as electron-acceptor are presented. The OLEDs based on these two emitters exhibited blue and sky-

blue emission with CIE of (0.15,0.16) and (0.15, 0.30), respectively. The maximum external quantum efficiency for the blue device reached 11.6% while for sky blue device it is 7.2%.