Excited state modulation in Donor-Substituted Multi-resonant Thermally Activated Delayed Fluorescence Emitters

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Abstract

Examples of multi-resonant thermally activated delayed fluorescence (MR-TADF) emitters that emit at longer wavelengths remain rare. To reach that goal, we decorate different numbers and types of electron-donors about a central MR-TADF core, **DiKTa**. Depending on the identity and number of donor groups, the excited state either remains short range charge transfer (SRCT) and thus characteristic of an MR-TADF emitter or becomes a long-range charge transfer (CT) that is typically observed in donor-acceptor TADF emitters. The impact is that in three examples, **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa**, which emit from a SRCT state, the emission remains narrow, while in four examples, **TMCz-DiKTa**, **DMAC-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa**, which emit via a CT state, the emission broadens significantly. Through this strategy, the organic light-emitting diodes fabricated with the three MR-TADF emitters show maximum electroluminescence emission wavelengths, λ_{EL} , of 511, 492 and 547 nm with moderate full-width at half maxima (FWHM) of 62, 61 and 54 nm, respectively. Importantly, each of these devices show high maximum external quantum efficiencies (EQE_{max}) of 24.4%, 23.0% and 24.4%, which are amongst the highest reported

with ketone-based MR-TADF emitters. OLEDs with D-A type emitters, **DMAC-DiKTa** and **TMCz-DiKTa**, also show high efficiencies, with EQE_{max} of 23.8% and 20.2%, but accompanied by broad emission at λ_{EL} of 549 and 527 nm, respectively. Noteworthy is that the **DMAC-DiKTa**-based OLED shows very small efficiency roll-off, and its EQE remains 18.5% at 1000 cd m⁻². Therefore, this work demonstrates that manipulating the nature and numbers of donor groups decorating a central MR-TADF core is a promising strategy for both red-shifting the emission and improving the performance of the OLEDs.

Introduction

Thermally activated delayed fluorescence (TADF) materials are a promising class of emitters for organic light-emitting diodes (OLEDs) as the devices can realise up to 100% internal quantum efficiency while the organic emitters can be easily synthesized at low cost and are sustainable.¹⁻³ TADF operates by converting non-emissive triplet excitons into singlets through endothermic reverse intersystem crossing (RISC). RISC is typically only possible when there is spin-orbit coupling (SOC) between the triplet and singlet states, and the energy gap between them (ΔE_{ST}) is small. The magnitude of ΔE_{ST} is correlated with the degree of overlap of the orbitals involved in the transition, which typically are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).⁴ The corresponding molecular design usually involves minimizing the conjugation between the electron-donating moieties and electron-accepting moieties by adopting a strongly twisted conformation between these two units. This commonly used design has a number of drawbacks. Due to the large redistribution of the electron density during the transition, the nature of the emission is charge transfer (CT) between the donor and acceptor.⁵ This, coupled with the conformational flexibility inherent in the design, leads to a broad emission spectrum (full width half-maximum, FWHM, of 80-200 nm).⁶ This significantly degrades the color gamut of the OLEDs, which is

an undesirable trait for displays. Therefore, there is at present a growing effort to develop TADF materials that show both a small ΔE_{ST} and narrow emission spectra.

One subclass of TADF emitters that responds to these criteria are multi-resonant TADF emitters (MR-TADF). Examples of MR-TADF emitters are shown in Figure S3. MR-TADF emitters are nanographenes containing suitably positioned electron-donating atoms (e.g., N, O, S) and electron-deficient atoms or groups (e.g., B, C=O) within the fused aromatic framework. In these compounds, electrons and holes are localized on adjacent atoms due to the complementary mesomeric effect of the electron-donating and electron-accepting units leading to the required small exchange integral and ΔE_{ST} .⁷ Although nearly 100 MR-TADF emitters have been reported since the first example in 2016,⁸ the majority of these show blue or green emission. There are still very few examples that emit at longer wavelengths.⁷ Therefore, this work focusses on developing longer wavelength MR-TADF emitters.

There are several potential strategies that may be employed to tune the emission energy towards the red. The first involves strategic placement of the relative positions of the electron-donating and electron-accepting groups. In 2020, Yasuda and co-workers,⁹ arranged two electron-donating nitrogen atoms *para* to each other and two boron atoms *para* to each other about the central phenyl ring (namely B- π -B and N- π -N), which led to a significantly red-shifted emission and is the first example of a red MR-TADF emitter, **BBCz-R**, showing an emission maximum, λ_{PL} , of 615 nm in toluene solution. Duan and co-workers,¹⁰ adopted a similar strategy, producing two red emitters, **R-BN** and **R-TBN**, with N- π -N arrangements (λ_{PL} = 662 and 692 nm in toluene solution). A second strategy involves extending the conjugation length of the MR-TADF emitter core. Hatakeyama and co-workers,¹¹ reported a green emitter (λ_{PL} of 506 nm in 1wt% PMMA film), **OAB-ABP-1**, that contains an extended π -skeleton that consists of an alternating pattern of *para*-disposed O-B-N atoms. Kido and co-workers¹² reported a

green emitter **PXZ-BN** with λ_{PL} of 502 nm by replacement of carbazole for phenoxazine within **BCz-BN** skeleton. In a similar vein, Yang and co-workers incorporated sulfur, affording the green emitter **2PTZBN** (λ_{PL} = 510 nm in toluene), with the expectation of enhancing spin-orbit coupling and hence the reverse intersystem crossing rate.¹³ A third strategy to modulate the emission involves the incorporation of peripheral electron-donating or electron-accepting moieties. Duan and co-workers,¹⁴ reported the first examples of green-emitting MR-TADF emitters (λ_{PL} = 502 nm in 6 wt% doped mCPCB film), **2F-BN**, by decorating peripheral electron-withdrawing fluorophenyl groups *para* to the central boron atom. Wang and co-workers, also employed the same strategy, incorporating electron-withdrawing benzonitrile units in the compound **(R)-OBN-4CN-BN**, obtaining a green emitter (λ_{PL} = 500 nm in toluene). Duan and co-workers,¹⁵ reported another green-emitting MR-TADF compound (**AZA-BN**) that incorporates a fused azaphenanthrene (λ_{PL} = 522 nm in toluene). Using the same **BCz-BN** skeleton, Wang and co-workers, reported the green emitter (***m*-Cz-BNCz**) that contains a *meta*-disposed auxiliary di-*tert*-butylcarbazole with respect to the central boron atom (λ_{PL} = 519 nm in toluene).¹⁶ Recently, Yang and co-workers, introduced donor groups at the *para* position of the carbazole of the **BCz-BN** skeleton and demonstrated color modulation from sky blue to yellow (λ_{PL} of 496 to 562 in toluene).¹⁷ Using the same **BCz-BN** skeleton, You and co-workers, combined both donor and acceptor groups located *para* to the N and B atoms, respectively, to realize orange emission (λ_{PL} of 581 nm in toluene).¹⁸ Although B/N-based emitters have realized full-colour emission, their synthesis can only be reached through lithiation–borylation–cyclization reaction or electrophilic fixed-point C–H borylation cyclization reaction, which complicates downstream elaboration of these structures. A second family of MR-TADF compounds employ electron-accepting carbonyl groups in lieu of boron atoms. We showed that decorating the MR-TADF **DiKTa** with mesityl groups, **Mes₃DiKTa**, can mitigate undesired aggregation caused quenching (ACQ) and excimer emission while also modestly

red-shifting the emission ($\lambda_{\text{PL}} = 468 \text{ nm}$ in toluene).¹⁹ We also reported a dimeric compound, **DDiKTa**, consisting of two **DiKTa** units, that showed a red-shifted emission with λ_{PL} of 500 nm.²⁰ Liao and co-workers, reported structurally rigid analogs of **DiKTa** that incorporated a carbon- oxygen- or sulfur-based tether. The compounds **DQAO**, **OQAO** and **SQAO** showed red-shifted emission compared to **DiKTa** with λ_{PL} ranging from 465 to 552 nm in toluene.²¹ Zhang and co-workers, reported the compounds **QAD-Cz**, **QAD-2Cz** and **QAD-mTPDA** that contain donor groups decorating the **DiKTa** core to afford D-A type emitters. These molecules showed blue to red emission with λ_{PL} ranging 488 to 586 nm in toluene solution.²²

In this context, we decorated the **DiKTa** core with different numbers of donors with differing electron-donating strengths. These donors include carbazole (Cz), 9,9-dimethylacridan (DMAC), carbazolyl-phenyl (Cz-Ph) and 1,3,6,8-tetramethyl-9*H*-carbazole (TMCz). These donors were positioned *para* to the central electron-donating nitrogen atom. We thus built a framework to systematically study the impact on the emission colour and nature of the excited state of the inclusion of these electron-donating groups (Figure 1). It was found that by introducing weak donors such as carbazole to the *para*-carbon position of nitrogen, the HOMO levels of the new emitters were destabilized significantly compared to that of the parent **DiKTa**, while the LUMO levels were barely perturbed, leading to the desired red-shifted emission. Importantly, the narrow emission characteristic of MR-TADF emitters was maintained. However, when the electron-donating strength was further increased, the emission nature changed to CT and the emission spectra significantly broadened. In this study, weaker-donor-based emitters, **Cz-DiKTa**, **3Cz-DiKTa** and **Cz-Ph-DiKTa** maintained their MR-TADF character in all the tested environments, while, stronger-donor-based emitters, **TMCz-DiKTa**, **DMAC-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** showed a more complicated behavior where CT emission dominates in polar media.

Figure 1. The molecular design of **DiKTa**-based MR-TADF emitters and their emission color. The compounds above the arrow contain stronger donors and emit via a long-range CT state and show broad emission while the compounds below the arrow contain weaker donors and emit via a SRCT state and show narrowband emission. The images are toluene solutions photoexcited at 365 nm.

Results and Discussion

Synthesis

Seven donor-substituted **DiKTa** emitters, **Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa**, **3Cz-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa**, were obtained following either palladium-catalyzed Buchwald-Hartwig amination or Suzuki-Miyaura cross-coupling with suitably brominated **DiKTa** intermediates as outlined in Scheme S1. The identity and purity of the seven emitters were ascertained using a combination of ^1H NMR and ^{13}C NMR spectroscopy, HRMS, HPLC and element analysis, and melting point determination.

Theoretical Studies

The frontier molecular orbitals (FMOs) of these emitters were firstly modelled based on the optimized ground state gas-phase geometry using Density Functional Theory (DFT) at the PBE0/6-31G(d,p) level of theory. The HOMO and LUMO distributions are shown in Figure S5 and the HOMO and LUMO level of the seven compounds are listed in the Table S1.

Compared to **DiKTa** (-5.94/-2.31 eV), the HOMO level is destabilized by 0.21 to 0.68 eV, and the degree of destabilization correlates with both the strength and numbers of the peripheral donor group. We noticed that the occupied orbital localized on the **DiKTa** core of the series of donor-substituted **DiKTa** compounds does not correspond to the HOMO, instead residing on the donor (see Figure S5). For the compounds with the weakest donors (**Cz-DiKTa**, **Cz-Ph-DiKTa**, **3Cz-DiKTa**) this orbital slightly delocalizes to the carbazoles, thereby resulting in destabilization compared to **DiKTa** while for the compounds containing the strongest donors (**TMCz-DiKTa**, **DMAC-DiKTa**, **3DMCz-DiKTa**) the energy of the **DiKTa**-localized orbital remains unaffected.

We then employed the Tamm-Dancoff approximation to time-dependent DFT (TDA-DFT) to predict the energies of the excited states (Table S1).²³⁻²⁴ TDA-DFT calculations predict that the nature of the lowest singlet excited state (S_1) of **Cz-DiKTa**, **3Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** is CT that is characteristic of D-A type TADF compounds as shown in Figure S5.¹⁹ However, we have previously demonstrated that it is essential to use suitably high-level theory models to accurately predict the excited state energies of MR-TADF compounds.⁶ Therefore, we employed Spin-Component Scaling Coupled-Cluster second-order approximate Coupled-Cluster (SCS-CC2) with the cc-pVDZ basis set to more accurately model the nature of the charge transfer excited states. Figure 2 shows the difference density plots of the S_1 and the second lowest singlet excited state (S_2) transitions of these emitters obtained using SCS-CC2. **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa** all exhibit similar S_1 difference density plot patterns akin to that for **DiKTa** (shown in Figure S7).¹⁹ Based on the charge-transfer distance, $D_{CT} < 1.4 \text{ \AA}$, we assign these excited states to be SRCT (Table S2). At the same time, small contributions to the difference density plots can be seen at the peripheral donor fragments in the new emitters, especially on the “top” carbazole moiety in **3Cz-DiKTa**. The S_2 state of each

of **Cz-DiKTa**, **TMCz-DiKTa** and **Cz-Ph-DiKTa** possesses $n-\pi^*$ character, while for **3Cz-DiKTa** S_2 remains a $\pi-\pi^*$ transition. The S_1 difference density plot of **DMAC-DiKTa** is almost identical to that of **DiKTa**, while the S_2 difference density plots shows a D-A type long range CT character as the increased density can be seen on the electron-deficient **DiKTa** core and the decreased density is located on the peripheral DMAC moieties. Indeed, the D_{CT} of this state is 3.18 Å, characteristic of a long-range CT state. Since all the calculations are carried out in gas-phase, potentially the nature of the emissive excited state may switch between MR-TADF CT and D-A CT, depending on the environment as the energy gap between the S_1 and S_2 ($\Delta E_{S_1S_2}$) of this emitter is small (0.34 eV) and the S_2 electrical dipole moment for the S_2 state is large. We also performed the same calculations on some reported donor-acceptor type emitters containing an MR-TADF moiety acting as the acceptor, to validate our computational methodology (Figure S4).²⁵ All the investigated emitters show SRCT S_1 states in the gas phase calculations and a narrow emission characteristic of a MR-TADF behavior. **ADBAN-Me-MesCz** and **DABNA-2** show large $\Delta E_{S_1S_2}$ of 0.71 and 0.64 eV at the SCS-CC2 level, which suggests that this $\Delta E_{S_1S_2}$ energy gap is large enough to prevent the switching of light emission from the SRCT state to the long-range CT state when considering the impact of solvent effects or polarization effects arising in the solid state. By contrast, **PXZ-DABOA**, **TDBAac**, **TDBA-DI** and **QAO-dic** all have predicted D-A type CT S_2 states, and much smaller $\Delta E_{S_1S_2}$ values of 0.04-0.29 eV. Such a small energy difference implies that a state inversion becomes possible when the medium is sufficiently polar. When considering **3DMCz-DiKTa** and **3DMAC-DiKTa**, the S_1 state shows a strong contribution of the hole density on the top Cz unit while the electron density is mainly localized on the **DiKTa** core, resulting in a long-range CT state. The calculated S_1/T_1 energies for the MR-TADF predicted emitters, **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa**, are 3.35/3.09, 3.39/3.13 and 3.05/2.81 eV, respectively, with corresponding ΔE_{ST} values of 0.26, 0.26 and 0.24 eV. These ΔE_{ST} values are of similar

magnitude to that of **DiKTa** (0.27 eV), and it indicates a likely similar TADF efficiency in these compounds. As **3TMCz-DiKTa** and **3DMAC-DiKTa** are predicted to be D-A dominant TADF emitters, the ΔE_{ST} obtained from the SCS-CC2 calculations are smaller (0.18 and 0.03 eV, respectively).

Figure 2. (a) Molecular structures and difference density plots of S_1 and S_2 excited states (calculated in the gas phase at the SCS-CC2/cc-pVDZ level) for **Cz-DiKTa**, **Cz-Ph-DiKTa**, **3Cz-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa**, **3DMCz-DiKTa** and **3DMAC-DiKTa**, f is the oscillator strength.

2.3 Optoelectronic Properties

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were used to experimentally determine HOMO and LUMO levels. The CV and DPV profiles in dichloromethane are shown in Figure 3a (**3TMCz-DiKTa** and **3DMAC-DiKTa** are shown in Figure S8) and the electrochemical data are summarized in Table S3. The CV profile of **Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa**, **3Cz-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** all show reversible reduction waves, which corresponds to the reduction localized on the **DiKTa** core. While **Cz-DiKTa** and **Cz-Ph-DiKTa** show irreversible oxidation

waves, which are assigned to the oxidation of the carbazole, when the donor is DMAC and TMCz, the oxidation waves become significantly more reversible. The $E_{\text{red}}/E_{\text{ox}}$ values of all seven emitters are determined from the peak of the DPVs. The LUMO levels of **Cz-DiKta**, **Cz-Ph-DiKta**, **TMCz-DiKta** and **DMAC-DiKta** are almost identical to that of **DiKta** (HOMO/LUMO values of -6.12/-3.00). When the numbers of donors are increased (**3Cz-DiKta**, **3TMCz-DiKta** and **3DMAC-DiKta**), the LUMO stabilizes by ca. 0.2 eV. In comparison, increasing the electron-donating strength of the peripheral donor (e.g., from Cz to DMAC) results in shallower HOMO levels. Similarly, increasing the number of electron donors also results in shallower HOMOs. Therefore, both strategies can be used to reduce the HOMO-LUMO band gap.

The room-temperature ultraviolet–visible (UV-Vis) absorption, steady-state photoluminescence (PL), recorded at room-temperature (SS RT), and PL spectra of the prompt and delayed emission recorded at 77 K, (the latter being the phosphorescent spectra) in toluene (10^{-5} M) are shown in Figures **3b-f** (Figure **S9** shows the PL spectra for **3TMCz-DiKta** and **3DMAC-DiKta**), the corresponding data are summarized in Table **S4**. The absorption spectra all show two characteristic absorption bands. The higher energy bands (300-430 nm) are attributed to π - π^* locally excited (LE) transitions of both the donors and the **DiKta** core, and the lower energy bands between 443-492 nm are attributed to SRCT transitions centered on the **DiKta** core that are characteristic of MR-TADF emitters. Compared to **DiKta**,¹⁹ the lowest-energy absorption band of the **Cz-DiKta**, **Cz-Ph-DiKta** and **3Cz-DiKta** progressively red-shifts and becomes broader and weaker as shown in Figure **3**, suggesting increasing CT character of the transitions associated with this band. The CT absorption bands of **TMCz-DiKta** and **DMac-DiKta** have lower molar absorptivity, which can be rationalized by the small FMO overlap due to the strongly twisted conformation of the bulky TMCz donor and the electron-donating strength of the DMAC donor. The seven compounds show a progressively

red-shifted emission with increasing number and strength of the electron-donors from 472 to 667 nm compared with **DiKTa** ($\lambda_{PL} = 460$ nm, FWHM= 27 nm). **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa** show small full width half maximum (FWHM) of 54, 47 and 53 nm, respectively. The small FWHM is correlated to the small Stokes shifts of 31-50 nm, which indicates that the structural relaxation is small in their excited states. In contrast, the Stokes shifts of **TMCz-DiKTa**, **DMAC-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** are much larger (86 to 242 nm) and the FWHM are greater than 80 nm. These results indicate that in the presence of strong electron-donating groups, the SRCT character of the excited state disappears and long-range D-A type CT character starts to be dominant. These observations agree with the computational results shown in the Figure 2. We next probed how the nature of the emissive excited state evolves as a function of solvent polarity and the results are presented in Figure S10. **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa** all show a small degree of positive solvatochromism that is characteristic of SRCT states associated with MR-TADF emitters.¹⁹ By contrast, **TMCz-DiKTa**, **DMAC-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** show significant positive solvatochromism, suggesting the lowest excited states of these compounds, especially in polar media, are CT in nature. They also show CT and SRCT dual emission in high polarity solvents, with emission moving from SRCT to CT with increasing polarity (Figure S10). This was observed previously using a MR-TADF core (**ADBNA-Me-Mes**), with NMe₂ substitution.²⁶

The ΔE_{ST} values were determined from the difference in energy of the onsets of the prompt fluorescence and phosphorescence spectra in toluene at 77 K. The corresponding ΔE_{ST} values of **Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa**, **3Cz-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** are 0.20, 0.22, 0.23, 0.21, 0.11, 0.01 and 0.01 eV, respectively. The ΔE_{ST} values of **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa** are consistent with the SCS-CC2 calculations, which implies the emissive excited state is SRCT in nature. **TMCz-DiKTa** shows

a broader emission spectrum but possesses an identical ΔE_{ST} value to the predicted one, which indicates that there may be mixed SRCT/CT character in low polarity solvents such as toluene. The calculated D-A type emitters **DMAC-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa**, show much smaller ΔE_{ST} values, which reflects the smaller overlap integral.

Figure 3. (a) Cyclic voltammogram (CV) and differential pulse voltammetry (DPV) in degassed DCM with 0.1 M $[n\text{Bu}_4\text{N}]\text{PF}_6$ as the supporting electrolyte and Fc/Fc^+ as the internal reference (0.46 V vs. SCE²⁷). Absorption and steady-state PL spectra obtained in toluene at RT (SS RT), prompt PL (1-100 ns) and phosphorescence spectra (1-10 ms) obtained in toluene glass at 77 K, measured by iCCD ($\lambda_{\text{exc}} = 340 \text{ nm}$) for (b) **Cz-DiKTa**, (c) **Cz-Ph-DiKTa**, (d) **TMCz-DiKTa**, (e) **DMAC-DiKTa** and (f) **3Cz-DiKTa**.

We next evaluated the photophysical properties of the seven emitters in dropcasted 1,3-bis(*N*-carbazolyl)benzene (mCP) films at a doping concentration of 2wt%. This host was chosen due to its high triplet energy of 2.81 eV,²⁸ and the photoluminescence quantum yield (Φ_{PL}) was found to be the highest at a concentration of 2 wt% (Tables S5 and S6). Indeed, **Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa** and **3Cz-DiKTa** films show high Φ_{PL} values of 90%, 77%, 71%, 72% and 78%, respectively. However, **3TMCz-DiKTa** and

3DMAC-DiKTa only present a Φ_{PL} of around 20%, which may be attributed to the much stronger CT band and relatively lower calculated oscillator strength for the CT states (*vide supra*). Further, their emission is red-shifted compared to the others, resulting in larger nonradiative decay processes. S_1 and T_1 levels in the doped film were determined from the onsets of the prompt fluorescence and phosphorescence spectra, respectively, measured at 77 K (Figure S11). The corresponding ΔE_{ST} values of **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa** are 0.14, 0.10 and 0.16 eV, respectively, which are slightly smaller than those measured in toluene glass. This may reflect changes in conformation upon slow cooling of the film in comparison to flash freezing of the toluene glass samples. **DMAC-DiKTa**, **TMCz-DiKTa**, **3TMCz-DiKTa** and **3DMAC-DiKTa** possess very ΔE_{ST} ranging from 0.01-0.08 eV.

Table 2. Photophysical data in 2 wt% doped mCP films.

Compound	λ_{PL} / nm	λ_{exc} / nm	FWHM ^b / nm	Φ_{PL} ^c / %	$\tau_{\text{p}}^{\text{d}}$, $\tau_{\text{d}}^{\text{d}}$ / ns; μs	T_1^{e} / eV	S_1^{f} / eV	$\Delta E_{\text{ST}}^{\text{g}}$ / eV
DiKTa^f	466	340	40	70	4.5, 168	2.55	2.75	0.20
Cz-DiKTa	502	340	54	90	8.4, 178	2.48	2.62	0.14
Cz-Ph-DiKTa	486	340	47	77	5.9, 155	2.53	2.63	0.10
TMCz-DiKTa	501	340	80	71	7.6, 52	2.56	2.64	0.08
DMAc-DiKTa	534	340	94	76	19.6, 7.6	2.61	2.57	0.04
3Cz-DiKTa	539	340	53	78	10.2, 287	2.25	2.41	0.16
3TMCz-DiKTa	577	340	110	18	22.1, 3.3	2.38	2.39	0.01
3DMAc-DiKTa	599	340	116	23	21.7, 2.4	2.32	2.33	0.01

^a Obtained at 300 K, $\lambda_{\text{exc}} = 340$ nm; ^b Full-width at half-maximum; ^c Calculated using an integrating sphere, under N_2 at $\lambda_{\text{exc}} = 340$ nm. ^d Measured at $\lambda_{\text{exc}} = 379$ nm and 300 K under vacuum; ^e Obtained from the onset of the PL spectrum measured at 77 K in a time window of 1 to 100 ns; $\lambda_{\text{exc}} = 343$ nm. ^f Obtained from the onset of the delayed spectrum (1-10 ms) at 77 K, $\lambda_{\text{exc}} = 355$ nm. ^g Obtained from the onset of the prompt spectrum (1-100 ns) at 77 K. ¹⁹ $\Delta E_{\text{ST}} = E(S_1) - E(T_1)$.

Figure 4. (a) PL spectra of **Cz-DiKTA**, **Cz-Ph-DiKTA**, **3Cz-DiKTA**, **TMCz-DiKTA**, **Cz-DiKTA**, **3TMCz-DiKTA** and **3DMAC-DiKTA** in 2 wt% doped mCP films at room temperature, $\lambda_{exc} = 340$ nm. (b) Time-resolved PL decays of **Cz-DiKTA**, **Cz-Ph-DiKTA**, **3Cz-DiKTA** and **TMCz-DiKTA** in 2 wt% mCP at room temperature, $\lambda_{exc} = 379$ nm; (c) Time-resolved PL decays curves of **DMAC-DiKTA**, **3TMCz-DiKTA** and **3DMAC-DiKTA** in 2 wt% doped mCP films at room temperature and $\lambda_{exc} = 379$ nm.

Figures 4b and 4c show the time-resolved PL decays of the 2 wt% doped mCP films. All PL decays show prompt and delayed emission components at room temperature. For **Cz-DiKTA**, **Cz-Ph-DiKTA** and **3Cz-DiKTA**, the prompt emission lifetimes, τ_p , are in the range of 8.4-10.2 ns, and the delayed emission lifetimes, τ_d , are between 155-287 μ s, which are of the same order of magnitude of that of the parent compound **DiKTA** (168 μ s) in 2wt% mCP doped film. The compound **TMCz-DiKTA** shows an intermediate delayed lifetime of 52 μ s, indicating that this compound possesses an excited state of intermediate character between D-A and SRCT in mCP. By contrast, **DMAC-DiKTA**, **3TMCz-DiKTA** and **3DMAC-DiKTA** show longer prompt emission lifetimes ranging from 19.6-22.1 ns and shorter delayed emission lifetimes of 2.4-7.6 μ s. The shorter delayed emission lifetime of these three emitters can be attributed to their smaller ΔE_{ST} values. The temperature-dependent time-resolved PL decays of all seven emitters (Figure S13) reveal the expected increase in the contribution of the delayed emission

component with increasing temperature, which corroborates the TADF nature of these compounds.

Organic light-emitting diodes

We next fabricated vacuum-deposited OLEDs only with **Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa** and **3Cz-DiKTa**, as these compounds possessed suitably attractive Φ_{PL} . Here we utilized a higher concentration of emitter (7.5 wt%) with the aim of improving the charge balance in the OLED device structure; we note that the photophysical behavior of the evaporated 7.5 wt% doped films in mCP is quite similar to that of the 2 wt% doped films in mCP, with only a small red-shift in the emission and a small decrease in Φ_{PL} (Figures S15 and Table S7). The optimized OLED structure is shown in Figure 5a and consists of: indium-tin-oxide (ITO) / 4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (TAPC, 40 nm/ mCP (10 nm)/ 7.5 wt% **emitter**:mCP (20 nm)/ 2,8-bis(diphenyl-phosphoryl)-dibenzo[b,d]thiophene, (PPT, 10 nm)/ 1,3,5-tri(*m*-pyridin-3-ylphenyl)benzene (TmPyPb, 50 nm)/ LiF (1 nm)/ Al (100 nm), where ITO acts as the transparent anode, TAPC acts as the hole-transporting layer, mCP acts as both the electron blocking layer and the host within the emissive layer, PPT acts as the hole blocking layer, TmPyPb acts as the electron transporting layer, LiF acts as the electron injection layer.

Figure 5. (a) Device configuration with energy levels and thicknesses for each layer, (b) Photographs of OLEDs under operation. (c) Commission Internationale de L'Éclairage diagram. (d) Current density versus voltage and luminance versus voltage curves. (e) Electroluminescence spectra. (d) External quantum efficiency (EQE) versus luminance curves.

Figure 5e illustrates the EL spectra of these devices. The OLEDs with **Cz-DiKTA**, **Cz-Ph-DiKTA**, **TMCz-DiKTA**, **DMAC-DiKTA** and **3Cz-DiKTA** show electroluminescence maxima, λ_{EL} , of 511, 492, 527, 549, and 547 nm, with corresponding Commission Internationale de l'Éclairage (CIE) coordinates of (0.24, 0.61), (0.18, 0.50), (0.32, 0.60), (0.40, 0.57) and (0.39, 0.60). The devices based on the MR-TADF emitters, **Cz-DiKTA**, **Cz-Ph-DiKTA** and **3Cz-DiKTA**, show narrow electroluminescence spectra with FWHMs of 62, 61 and 54 nm which are slightly broader than that of **DiKTA** (39 nm).¹⁹ The FWHM values are larger for the devices with **TMCz-DiKTA** and **DMAC-DiKTA** (78 to 89 nm), respectively. This reflects CT emission in these devices in line with that observed in the PL spectra. Overall, the EL emission of the devices can be tuned from sky blue to yellow green by regulating the number and the electronic-donating strength of peripheral donor around the **DiKTA** core.

Table 2. Summary of OLED performance

Emitters	λ_{EL} /nm	FWHM ^a /nm	V_{on} ^b / V	L_{max} ^c /cd m ⁻²	EQE /% ^d max/100/1000	PE _{max} ^e /lm W ⁻¹	CIE ^f
Cz-DiKTa	511	62	3.2	13260	24.9/20.4/13.0	68.9	0.24, 0.61
Cz-Ph-DiKTa	492	61	3.2	8529	23.0/19.3/10.2	52.3	0.18, 0.50
TMCz-DiKTa	527	78	3.1	21758	20.2/19.6/16.7	60.0	0.32, 0.60
DMAC-DiKTa	549	89	3.1	35506	23.8/22.3/19.9	78.6	0.40, 0.57
3Cz-DiKTa	547	54	3.2	10796	24.4/17.3/6.2	83.1	0.39, 0.60

^a Full width at half maximum of the EL spectrum. ^b The turn-on voltage at the luminance of 1 cd m⁻². ^c luminance. ^d Maximum external quantum efficiency/EQE at 100 cd m⁻²/EQE at 1000 cd m⁻². ^e Current efficiency; ^f Commission Internationale de L'Éclairage coordinates.

As depicted in Figure 5f, the devices with **Cz-DiKTa**, **Cz-Ph-DiKTa**, **TMCz-DiKTa**, **DMAC-DiKTa** and **3Cz-DiKTa** show very high EQE_{max} of 24.9%, 23.0%, 20.2%, 23.8% and 24.4%, respectively, which is much higher than that of the **DiKTa**-based device with **DiKTa** (14.7%) reported by our group.¹⁹ Considering the measured Φ_{PL} of the doped films fabricated by thermal evaporation (see Table S7) and assuming 25% outcoupling efficiency, the EQE_{max} of these devices are expected to be, respectively, 19.3%, 17.3%, 14.3%, 15.5% and 18.5%, which are much lower than the observed EQE_{max}. One potential explanation would be if the transition dipole of the emitters were horizontally oriented parallel to the substrate surface, as this could lead to higher amount of the out-coupled light from the OLEDs to air.² We therefore measured the molecular orientations of evaporated doped films of the emitters, which are identical to the ones used in the OLEDs. The angular dependent PL measurement results of these films are shown in Figure S18 and the anisotropy factors, a , extracted from the p-polarized emission

were found to be 0.33 for **Cz-DiKTa**, 0.36 for **Cz-Ph-DiKTa**, 0.37 for **TMCz-DiKTa**, 0.36 for **DMAc-DiKTa** and 0.30 for **3Cz-DiKTa**. These values are very close to the anisotropy factors of isotropically oriented emitters (0.33). Considering the device structure and the measured anisotropy factors, the corresponding simulated outcoupling efficiencies of these devices are, respectively, 25.4%, 24.4%, 23.2%, 23.0% and 25.4% (See SI for the details of the calculation and Table S10). Combining the measured Φ_{PL} of the films and the simulated outcoupling efficiencies, the EQE_{max} values were expected to be 19.6%, 16.8%, 13.1%, 14.3% and 18.8%, respectively, which are lower than the observed values. Therefore, the emitter orientation alone cannot explain this discrepancy. Similar higher than expected performance was also found in many other MR-TADF emitters.^{22, 29-30} Among these works, a group of structurally related emitters, **QAD-Cz**, **QAD-2Cz** and **QAD-mTDPA**, reported recently by Zhang and co-workers, showed near unity Φ_{PL} values of 99.6%, 99.5% and 97.2% in mCP doped film, respectively, and EQE_{max} of the corresponding OLEDs of 20.3%, 27.3% and 23.9%, respectively, which implies outcoupling efficiencies of 20.4%, 27.4% and 27.1%, respectively.²² These EQE_{max} values are also higher than 20%. Unfortunately, the anisotropy factors of these materials were not measured in the paper and the out-coupling efficiency was not discussed.

Although the origin of our higher-than-expected EQE_{max} is not clear, we can envisage two potential causes (see “Out-coupling efficiency simulation and possible explanation about higher experimental EQE than predicted EQE” in SI). The first is that the emission efficiency of our emitters might be underestimated due to some oxygen remaining in the integrating sphere during our measurements of the Φ_{PL} ; also, in the OLED stack, emission efficiency can be enhanced by the Purcell effect. The second potential explanation could be microcavity effects in the OLED stack leading to light emission that is directed forwards more than for a Lambertian emitter and hence increasing the apparent EQE when measured in the forward

direction. As the main focus of this work is to demonstrate the impact of donor substitution about **DiKTa**-type MR-TADF compounds and how it modulates the nature of the CT character of the emitters and affects the performance of the OLEDs, the origin of the apparently high out-coupling efficiency will be investigated in future work.

In addition to the high EQE_{max} , these devices also show suppressed efficiency roll-off. The EQE values at 100 cd m^{-2} (EQE_{100}) for the **Cz-DiKTa**, **Cz-Ph-DiKTa** and **3Cz-DiKTa** devices are 22.5%, 19.2%, 17.8%, respectively, corresponding to an efficiency roll-off of 9.6%, 16.5% and 27.0%, respectively. This performance is improved compared to the **DiKTa**-based OLED (44% reported by us¹⁹ and 54% reported by Liao and co-workers²⁹). The EQE_{1000} values, however, drop dramatically with efficiency roll-off of between 50%-74%, which is not uncommon in MR-TADF-based OLEDs such as **Mes₃DiKTa** and the **DABNA-1**.^{8, 19} Serious efficiency roll-off also was observed in the devices with **QAD-Cz**, **QAD-2Cz** and **QAD-mTDPA**, where the EQE dropped to 0.73%, 12.4% and 4.7% at 1000 cd/m^2 , representing an efficiency roll-off greater than 55%. By contrast, for the devices with our D-A type TADF emitters, the EQE_{1000} for the OLEDs based on **DMAC-DiKTa** and **TMCz-DiKTa** are 19.9% and 16.7%, these show a much smaller efficiency roll-off of 16.4% and 17.3%, which can be attributed to the smaller ΔE_{ST} values. The OLED using the previously reported D-A emitter, **QAO-DAd**, and similar device structure also showed a comparable efficiency roll-off of 19.2% at 1000 cd/m^2 (EQE_{max} of 23.9% and EQE_{1000} of 19.3%). Due to the small efficiency roll-off observed in the **DMAC-DiKTa** device, a very high maximum brightness, L_{max} , of 35500 cd m^{-2} was reached (Figure 4c). The device performances reported in the present study are amongst the best results in ketone-containing MR-TADF devices (and devices containing a ketone-containing MR-TADF core as the acceptor in D-A emitters). Moreover, we demonstrate the importance of the choice of peripheral donor in order to maintain the MR-TADF character of the emitters.

Conclusions

In summary, through attaching different numbers of donors with different electron-donating strengths at the *para* position to the central nitrogen atom of the previous reported **DiKTa** core, the character of the charge transfer excited state can be modulated from SRCT to long-range CT. This change in the nature of the emissive excited state is reflected in a broadening and a bathochromic shift of the emission. The photophysical properties, corroborated by SCS-CC2 calculations, show that the introduction of strongly electron-donating donor moieties to the periphery of the **DiKTa** core leads to a destabilization of the HOMO and an enhancement of the long-range CT character of the emitters. It is noteworthy that the SRCT character that is emblematic of MR-TADF compounds is conserved with the introduction of weak donors (Cz, Cz-Ph) and so the color purity of these emitters is high. As a result, we achieved narrowband emission beyond 547 nm (FWHM = 54 nm) in the OLED accompanied by a high EQE_{max} of 24.4% from the device with **3Cz-DiKTa**. The **Cz-DiKTa** OLED exhibited the highest EQE_{max} of 24.9% at λ_{EL} of 511 nm. The OLED with the D-A type emitter **3DMAC-DiKTa** showed high EQE_{max} of 24.3% and a small roll-off of 18.5% at 1000 cd m⁻². The strategy of judiciously decorating the MR-TADF core with weak donating groups is a useful tool to modulate the photophysical properties of these emitters and to realize high-performance OLEDs. However, too strong a choice of donor leads to the generation of donor-acceptor compounds, which leads to red-shifted and broadened emission in the device.

Supporting Information

¹H and ¹³C NMR spectra, HRMS and HPLC of all target compounds; supplementary computational data; supplementary photophysical data, supplementary devices data, and orientation measurement data.

Acknowledgments

S.W. thanks the China Scholarship Council (201906250199). EZ-C and IDWS acknowledge support from EPSRC (EP/L017008, EP/P010482/1). We are also grateful for financial support from the University of St Andrews Restarting Research Funding Scheme (SARRF) which is funded through the Scottish Funding Council grant reference SFC/AN/08/020. EZ-C is a Royal Society Leverhulme Trust Senior Research fellow (SRF\R1\201089). We would also like to thank the Leverhulme Trust (RPG-2016-047) for financial support. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska Curie grant agreement No 838885 (NarrowbandSSL). S.M.S. acknowledges support from the Marie Skłodowska-Curie Individual Fellowship. Computational resources have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifiques de Belgique (F.R.S.-FNRS) under Grant No. 2.5020.11, as well as the Tier-1 supercomputer of the Fédération Wallonie-Bruxelles, infrastructure funded by the Walloon Region under the grant agreement n1117545. Y.O. acknowledges funding by the Fonds de la Recherche Scientifique-FNRS under Grant n° F.4534.21 (MIS-IMAGINE). D.B. is a FNRS Research Director.

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