Improving Efficiency Roll-off in Multi-Resonant Thermally Activated Delayed Fluorescent OLEDs Through Modulation of the Energy of the $T_2$ State

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Abstract: The $S_1$ state and high-lying triplet excited states ($\Delta E_{S_1T_2}$) offers insight into clarifying the mechanism of efficiency roll-off of organic light-emitting diodes (OLEDs). However, experimental detection of the $\Delta E_{S_1T_2}$ is challenging due to Kasha’s rule. Here, we report two emitters, PhCz-O-DiKTa and PhCz-DiKTa, showing multi-resonant thermally activated delayed fluorescence (MR-TADF). By modulating the conjugation between the MR-TADF DiKTa emissive center and donor substituent, emission directly from the $T_2$ state was for the first time observed in MR-TADF emitters. Single crystal and reduced density gradient (RDG) analyses reveal that the origin of the reduced observed concentration-quenching results from weak CH...π and slipped π...π stacking interactions, which suppress nonradiative transitions. Theoretical and photophysical investigations reveal that the $\Delta E_{S_1T_2}$ difference influences the reverse intersystem crossing (RISC) rate. The OLEDs employing PhCz-O-DiKTa and PhCz-DiKTa as emitters show maximum external quantum efficiencies (EQE$_{\text{max}}$) of over 20%, but very different efficiency roll-off behavior (54.5% vs 13.6% at 100 cd m$^{-2}$). Thus, this design provides a possible solution to mitigating device efficiency roll-off by designing MR-TADF emitters with degenerate $S_1$ and $T_2$ states.

Keywords. multi-resonant thermally activated delayed fluorescence (MR-TADF), emissive $T_2$ state, narrowband emission, conjugation modulation, organic light-emitting diodes
Introduction

Organic light-emitting diodes (OLEDs) are surging in use across multiple markets such as those of wearable electronics, smartphones, flat displays, and solid-state lighting. This is largely driven by their numerous promising advantages compared to conventional liquid crystal displays (LCDs), such as lower cost, greater flexibility, better picture quality and fast response time.\(^1\) Fabrication of high-performance OLEDs is paramount to the success of these applications. Fluorescent OLEDs can only convert 25% of singlet excitons into emission, with the loss of 75% triplet excitons as heat.\(^2\) In the past decade, thermally activated delayed fluorescence (TADF) materials have emerged as emitters for the third-generation OLED, able to harvest 100% of excitons to generate light, at comparable exciton utilization efficiencies to phosphorescent OLEDs. Generally, TADF emitters are based on a strongly twisted donor-acceptor (D-A) design motif to electronically separate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) that results in a small energy gap between \(S_1\) and \(T_1\) states (\(\Delta E_{SIT1}\)).\(^{3-5}\) However, a relatively large nuclear reorganization and charge-transfer (CT) transition in the excited state unavoidably produce a broad emission band, reflected by a large full width at high maximum (FWHM) of around 100 nm.\(^6\) These undesired properties in D-A TADF emitters restrict their practical application in high-resolution displays where the color point requirements demanded by industry are difficult to obtain using materials showing broad emission.

At present, commercialized high-resolution OLED displays mainly employ a color filter or microcavity to reach the color purity required by broadcasting standards, which is inevitably accompanied by losses in device efficiency and energy utilization.\(^7\) Therefore, it would be of great utility to devise an emitter showing narrowband emission. Recently, Hatakeyama et al. introduced a subclass of TADF emitters coined multi-resonant TADF (MR-TADF), that show the desired narrowband emission. This is due to their rigid polyaromatic hydrocarbon (PAH) framework,\(^8\) where the rigid molecular skeleton and the short-range CT (SRCT) nature of the emissive singlet excited state enable simultaneously narrowband emission and small \(\Delta E_{SIT1}\). In this design, the electron densities of the HOMO and LUMO are localized on the adjacent atoms. Typically, boron/nitrogen (B/N) doped PAHs have emerged as the dominant design. For example, Hatakeyama and co-workers designed a B/N-doped MR-TADF compound, \textbf{v-DABNA}, that shows very narrowband emission (FWHM of 18 nm) at a photoluminescence (PL) maximum (\(\lambda_{\text{PL}}\)) of 467 nm, with a PL quantum yield (\(\Phi_{\text{PL}}\)) of 90%, and where the device's maximum external quantum efficiency (EQE\(_{\text{max}}\)) was an impressive 34.4%.\(^9\) A hyperfluorescence (HF) strategy has been extensively employed to mitigate


efficiency roll-off in the device, wherein generally a TADF emitter serves as the assistant dopant to efficiently harvest excitons and then these are efficiently transferred to the terminal emitter, a compound showing narrowband emission and with a fast radiative rate constant, $k_r$.\cite{10} Benefitting from these pioneering works, Lee and co-workers reported a hyperfluorescence (HF) device that showed an EQE$_\text{max}$ of 33.5% and a long operational device lifetime (LT$_{50}$, 50% of initial luminance) of 9500 hours at 100 cd m$^{-2}$ by employing v-DABNA as the terminal emitter and a triazine derivative PPCzTrz as the assistant dopant;\cite{11} the device with only v-DABNA as the emitter was much less stable (LT$_{50}$ = 31 hours).\cite{9} A similarly themed report by Adachi and co-workers documented an HF device using v-DABNA as the terminal emitter with an EQE$_\text{max}$ of 41% and a LT$_{50}$ > 10,000 hours.\cite{12} Besides HF, other strategies have been explored to improve the performance of MR-TADF OLEDs.\cite{13-18} For instance, Yang and co-workers proposed an effective strategy for mitigating aggregation-caused quenching (ACQ) by introducing sterically bulky groups onto a B/N-doped emitter.\cite{13}

Carbonyl (C=O)/N-doped PAHs are a second family of MR-TADF emitters.\cite{19-24} Initial studies by Yuan et al. and us using DiKTa (Figure 1a) derivatives documented the potential of this design,\cite{21, 25} however, the devices typically suffered from significant efficiency roll-off (> 30%) at 100 cd/m$^{-2}$ and low maximum luminance (L$_\text{max}$ ≤ 13,000 cd/m$^2$). Recently, we demonstrated that by decorating DiKTa with various donors, the OLEDs showed an improved EQE$_\text{max}$ and reduced efficiency roll-off compared to the device with the parent emitter;\cite{26} however, this improvement in efficiency roll-off was not present beyond 100 cd/m$^2$. Similarly, Zhang and co-workers reported three C=O/N-doped PAHs, QAD-Cz, QAD-2Cz, and QAD-mTDPA.\cite{27} Although having very similar molecular structures and near unity $\Phi_\text{PL}$, there is a stark dichotomy in the observed efficiency roll-off at 100 cd/m$^2$ (QAD-Cz: 73.4%, QAD-2Cz: 12.5%, and QAD-mTDPA: 51.0%). These results provide insight that a high-lying triplet excited state (T$_n$) is likely responsible for the differences in reverse intersystem crossing rate constants, $k_{\text{RISC}}$, and thus the different efficiency roll-off profiles. Improved MR-TADF design can be realized if we were above to experimentally determine the energy of these close-lying triplet states to the S$_1$ state. The employment of transient absorption spectroscopy can be used to detect the existence of T$_n$ states,\cite{28} but it lacks the capability of quantifying the energy of these states. Very recently, transient electron paramagnetic resonance spectroscopy (EPR) was employed by Evans and co-workers to reveal that multiple triplet excited states aid to mediate delayed fluorescence.\cite{29} In our previous work, we utilized transient EPR to distinguish the T$_2$ and T$_1$ states of the anthracene derivative DPAAnCN and revealed that exciton harvesting proceeded by a hybridized local and charge-transfer
(HLCT) fluorescence mechanism. Despite these advances, it remains challenging to map out the triplet state landscape.

We recently demonstrated using time-resolved PL spectroscopy that higher-lying triplet states could be observed in multiple-phosphorescence emitters.\cite{30-31} Capitalizing on this design paradigm, here we utilize conjugation modulation as a tool to brighten the T$_2$ state of MR-TADF emitters. We report two DiKTa derivatives PhCz-O-DiKTa and PhCz-DiKTa (Figure 1a), and explore the impact of conjugation from the decorated donor moiety on the efficiency roll-off of the OLED (Figure 1b); in the conceived emitter design the degree of conjugation between 9-phenyl-9H-carbazole (PhCz) and DiKTa is employed to regulate the vibronic coupling between two triplet excited states and activate emission from the T$_2$ state; PhCz acts as a perturbator of the energy of the T$_2$ state to tune $k_{\text{RISC}}$ (Figure 1c). The $\Phi_{\text{PL}}$ values as a function of doping level reveal that both emitters are reasonably resistant to concentration quenching. The existence of the T$_2$ state was demonstrated by time-resolved PL measurements and further confirmed by the observable T$_2$ afterglows. The OLED devices employing PhCz-O-DiKTa and PhCz-DiKTa as emitters indicate 100% exciton utilization assuming a 25% out-coupling efficiency. Similar $\text{EQE}_{\text{max}}$ (PhCz-O-DiKTa: 20.0%; PhCz-DiKTa: 22.0%) values were obtained; however, there is a stark contrast in efficiency roll-off at 100 cd/m$^2$ (PhCz-O-DiKTa at 54.5% and PhCz-DiKTa at 13.6%).

![Figure 1](image_url)

**Figure 1.** (a) Chemical structures of MR-TADF building blocks (PhCz and DiKTa) and the emitters (PhCz-O-DiKTa and PhCz-DiKTa) investigated in this work. (b) Schematic illustration of simplified Jablonski diagrams outlining the origin of the narrowband emission in MR-TADF emitters. (c) Schematic illustration of T$_2$-regulated RISC in MR-TADF emitters; Exc: Excitation; F: Fluorescence; DF: Delayed fluorescence.

**Results and discussion**
**Synthesis and structural characterization**

PhCz-O-DiKTa and PhCz-DiKTa were synthesized via Ullmann condensation and Suzuki-Miyaura coupling reactions using PhCz and DiKTa as building blocks. The synthetic routes are outlined in Scheme S1. All samples were purified via silica column chromatography followed by temperature-gradient vacuum sublimation. A combination of ¹H & ¹³C nuclear magnetic resonance spectroscopy (NMR), high-resolution mass spectrometry (HRMS), melting point determination, high-performance liquid chromatography (HPLC), elemental analysis (EA), and single-crystal X-ray diffraction were used to confirm the molecular structures and assess their purity (Figures S1-S13, Table S1).

**Theoretical Modelling**

![Figure 2](image.png)

**Figure 2.** (a) Electron density distributions and energy levels of the frontier molecular orbitals (isovalue: 0.02) calculated at the PBE0/6-31G(d,p) level. (b) Difference density plots (isovalue: 0.001) and excitation energy levels of excited states calculated in the gas phase at the SCS-ADC(2)/cc-pVDZ level; blue and green denote increasing and decreasing electron densities in the excited state compared to the ground state, respectively; f indicates oscillator strength.

First, the photophysical properties of PhCz-O-DiKTa and PhCz-DiKTa were modelled using density functional theory at the PBE0/6-31G(d,p) level. As shown in Figure 2a, PhCz-O-DiKTa and PhCz-DiKTa possess lowest unoccupied molecular orbitals (LUMOs) of similar energy and character, reflected by the DiKTa-localized density distribution. A slight energy difference between the highest occupied molecular orbitals (HOMOs) of the two compounds was observed, where the HOMO is localized on the PhCz subunit in PhCz-O-DiKTa but destabilized in PhCz-DiKTa due to the
extended π-conjugation possible in this compound. Time-dependent (TD) DFT calculations within the Tamm-Dancoff approximation (TDA)\textsuperscript{34} performed at the same level of theory predict that PhCz-O-DiKTa has a larger spin-orbit coupling constant between the S\textsubscript{1} and T\textsubscript{1} states at the optimized S\textsubscript{1} geometry than PhCz-DiKTa (0.43 cm\textsuperscript{-1} vs 0.10 cm\textsuperscript{-1}) but similar oscillator strength (0.11 vs 0.12), and both exhibit a relatively large energy gap between S\textsubscript{1} and T\textsubscript{1}, ΔE\textsubscript{S1T1} > 0.4 eV, (Figure S14a), which implies that neither compound will show TADF. Calculated vertical excitations to the S\textsubscript{1} state predict that the character of this state in both compounds is hybridized local and CT (Figure S14b). We have previously demonstrated the importance of using wavefunction-based methods to accurately model the excited state energies and ΔE\textsubscript{S1T1} of MR-TADF emitters,\textsuperscript{35-36} thus, we computed the energies of low-lying singlet and triplet excited states using spin-component scaling second-order algebraic diagrammatic construction (SCS-ADC(2)) functional with the cc-pVDZ16 basis set (Figure 2b).\textsuperscript{37} The calculation data are summarized in Table S2. As anticipated, a somewhat reduced ΔE\textsubscript{S1T1} (~ 0.25 eV) exists in both PhCz-O-DiKTa and PhCz-DiKTa. The S\textsubscript{1} oscillator strength of both compounds is over 0.24, reflecting a highly emissive state. The calculated distance (d\textsubscript{CT}) of the S\textsubscript{1} state of DiKTa is 0.803 Å (Table S1). A similar d\textsubscript{CT} exists in PhCz-O-DiKTa (0.944 Å), but a larger value is recorded for PhCz-DiKTa (1.292 Å) due to the π-conjugated geometry. Nevertheless, difference density plots of the four lowest-lying excited states reveal a remarkably SRCT localized on the DiKTa core (Figure 2b). Such a small reorganization of the electron density in the S\textsubscript{1} state is expected to translate into a narrowband emission. The difference density plots for PhCz-O-DiKTa and PhCz-DiKTa, are similar to that of DiKTa (Figure S15), thus demonstrating that the incorporation of PhCz only causes a perturbation of the excited-state energies without remarkably influencing the nature of the low-lying excited-states. Notably, although a ΔE\textsubscript{S1T1} of ~ 0.25 eV has been predicted, it remains challenging to achieve fast k\textsubscript{RISC} at 298 K with this energy gap as according to the Boltzmann distribution, the approximate exciton ratio between the S\textsubscript{1} and T\textsubscript{1} is 6.0 × 10\textsuperscript{5} : 1. Thus, to promote RISC in these compounds, a higher-lying triplet excited state T\textsubscript{2} of different orbital type to the S\textsubscript{1} state must be implicated to enable second-order coupling.\textsuperscript{28} The calculations predict that the S\textsubscript{1} and T\textsubscript{2} states of the two emitters are dominated by SRCT and n-π\textsuperscript{b} transitions (Figure 2b), respectively. PhCz-DiKTa possesses a smaller ΔE\textsubscript{S1T2} than that of PhCz-O-DiKTa (0.21 eV vs 0.08 eV) (Figure 2b). Therefore, we can reasonably expect that faster k\textsubscript{RISC} and shorter TADF lifetime (τ\textsubscript{DF}) occur in PhCz-DiKTa than in PhCz-O-DiKTa via second-order spin-vibronic coupling. As a result, it is vital to experimentally detect the T\textsubscript{2} energy to clarify the RISC processes.
Figure 3. (a) Cyclic and differential pulse voltammograms in degassed DCM with 0.1 M [\text{[nBu}_4\text{N}]PF_6 as the supporting electrolyte and Fc/Fc' as the internal reference (0.46 V vs. SCE).[^38] (b) UV-vis absorption and steady-state PL spectra recorded in aerated toluene at 298 K. Prompt (1-100 ns, \(\lambda_{\text{exc}} = 375\) nm) and delayed (3-100 ms, \(\lambda_{\text{exc}} = 350\) nm) PL spectra of (c) PhCz-O-DiKTa and (f) PhCz-DiKTa in 2-MeTHF at 77 K (\(\lambda_{\text{exc}} = 350\) nm); concentration: 1 \(\times\) 10^{-5} M. Solvatochromic PL study of (d) PhCz-O-DiKTa and (e) PhCz-DiKTa at 298 K in air (\(\lambda_{\text{exc}} = 350\) nm); inset: photos showing luminescence excited by a 365 nm UV torch.

**Optoelectronic characterization in solution**

We next investigated the optoelectronic properties in dilute solution. The energies of FMOs were inferred from the electrochemistry, where oxidation and reduction potentials (\(E^{\text{ox}}/E^{\text{red}}\)) were obtained using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in deaerated dichloromethane (DCM) with 0.1 M [\text{[nBu}_4\text{N}]PF_6 as the supporting electrolyte. The electrochemical data are presented in Table S3. The \(E^{\text{ox}}/E^{\text{red}}\) values of PhCz-O-DiKTa and PhCz-DiKTa determined from the DPV peaks, are 1.26/-1.34 V and 1.27/-1.35 V, respectively, vs SCE (Figure 3a), with corresponding HOMO/LUMO values of -5.60/-3.00 eV and -5.61/-2.99 eV, respectively. The similar FMO energies disclose the almost identical electronic configurations of the HOMO and LUMO in these two compounds. The slightly different FMO energies of PhCz-O-DiKTa and PhCz-DiKTa
compared to those of DiKTa (HOMO = -5.93 eV, LUMO = -3.11 eV)\(^{[25]}\) result from the weak electron-donation of the PhCz donor with the DiKTa core.

UV-vis absorption spectra of the two emitters in toluene reveal a relatively intense SRCT transition at ~ 450 nm (Figure 3b). Compared to DiKTa\(^{[25]}\), PhCz-O-DiKTa possesses a similar absorption coefficient (\(\varepsilon < 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\)) around 300-400 nm, which is highly enhanced in PhCz-DiKTa due to the \(\pi\)-conjugated geometry. At 298 K, narrowband emissions were evidenced in the steady-state PL spectra of PhCz-O-DiKTa and PhCz-DiKTa, with \(\lambda_{\text{PL}}\) at 478 nm and 490 nm and full widths at half maxima (FWHMs) of 39 nm and 55 nm (Figure 3b), respectively. The narrower and slightly blue-shifted emission of PhCz-O-DiKTa results from the \(\pi\)-conjugation-breaking geometry, which restricts the electronic coupling between PhCz and DiKTa. This is reflected by the larger interplanar angle between PhCz and DiKTa in PhCz-O-DiKTa (71.07°) versus PhCz-DiKTa (21.95°), based on the optimized S\(_1\) geometry (Figure S16a). PL lifetimes (\(\tau_{\text{PL}}\)) of PhCz-O-DiKTa and PhCz-DiKTa recorded at the emission maximum in air are 7.7 ns and 7.0 ns (Figure S17a), respectively, which increase to 8.6 ns and 8.7 ns under N\(_2\) (Figure S17b), respectively. From Figures 3d and 3e, a more pronounced positive solvatochromism is observed in PhCz-DiKTa, which reflects the larger degree of conjugation of the PhCz ground and its perturbation of the SRCT state to have more long-range CT (LRCT) character; this is also substantiated by a larger calculated S\(_1\) \(d_{\text{CT}}\) (1.292 Å) compared with that of PhCz-O-DiKTa (\(d_{\text{CT}} = 0.944 \text{ Å}\)). The emission of PhCz-O-DiKTa at ~ 400 nm in DMF is ascribed to LE emission (Figure 3d). In degassed toluene, steady-state PL intensities of the two emitters are both enhanced compared to those recorded in aerated toluene (Figure S18). \(\Phi_{\text{PL}}\) values of PhCz-O-DiKTa and PhCz-DiKTa in aerated toluene are 62% and 45%, which improve to 71% and 61%, respectively, demonstrating the contribution from triplet excitons (Figure S19). The \(\Delta E_{\text{S1T1}}\) values of PhCz-O-DiKTa and PhCz-DiKTa were estimated to be 0.36 eV, from the difference in energy of the onset of prompt and delayed emission spectra in 2-methyltetrahydrofuran (2-MeTHF) glass at 77 K (Figures 3c and 3f). The photophysical data are summarized in Table S4. The magnitude of this \(\Delta E_{\text{S1T1}}\) implies that TADF is not operational in these compounds. Reminiscent of the design model (Figure 1c) and theoretical calculations (Figure 2b), the higher-energy emission band probably originates from a higher degenerate triplet excited state, here defined as the T\(_2\) state, which is expected to be the bridge for TADF occurrence in this design.
Figure 4. (a) X-ray single crystal structures of PhCz-O-DiKTa and PhCz-DiKTa; ellipsoids are drawn at the 50% probability level for isolated molecules; intermolecular H···centroid and centroid···centroid distances are presented between adjacent molecules (distances in Å). (b) RDG mapped with isosurfaces (isovalue: 0.5) showing intermolecular interactions based on the dimers from single crystals.

Analysis of intermolecular interactions

Prior to investigating the photophysical in the solid state, we first studied the X-ray single crystal structures of PhCz-O-DiKTa and PhCz-DiKTa to elucidate what influence if any intermolecular interactions would have on the photophysics; interactions that would be present at high doping concentration in the film state. From Figure 4a, PhCz-O-DiKTa exhibits a larger interplanar angle (83.09°) between the PhCz and DiKTa subunits than PhCz-DiKTa (32.02°) due to the presence of the sp3-hybridized oxygen atom (Figure S16b). As a result of the more twisted geometry, PhCz-O-DiKTa exhibits weaker π···π stacking interactions than PhCz-DiKTa in the dimer (Figure 4a), although they do act in a mutually supportive manner. PhCz-O-DiKTa packs in a head-to-tail manner, but each end of the molecule interacts with a separate neighboring molecule, leading to the formation of weakly interacting chains. The more planar PhCz-DiKTa also displays a head-to-tail intermolecular stacking pattern, but with both head and tail of the molecule interacting with the same neighbor, and thus strengthens molecular electronic coupling between adjacent emitter molecules, and broadens the PL. The reduced density gradient (RDG) analysis using the Multiwfn program[39] corroborates the existence of intermolecular Van de Waals interactions as well as weakly repulsion steric interactions (Figure 4b), which are beneficial to restricting molecular motions.
Figure 5. PL spectra of (a) 10 wt% PhCz-O-DiKTa and (b) 10 wt% PhCz-DiKTa in mCP at 298 K; SS: steady-state PL in air; prompt PL in air: 10-20 ns; delayed PL in vacuum: 1-10 ms for PhCz-O-DiKTa and 0.2-2 ms for PhCz-DiKTa; inset: photos showing luminescence excited by 365 nm UV torch. (c) Time-resolved PL decay profile in vacuum at 298 K. (d) Total ΦPL and corresponding contributions from prompt and delayed components. Prompt (10-20 ns, λexc = 375 nm) and delayed (1-10 ms, λexc = 350 nm) PL spectra of (e) PhCz-O-DiKTa and (f) PhCz-DiKTa in vacuum at 77 K.

Photophysical investigations in the solid state

We next turned our attention to the photophysical characterization in an OLED-relevant host matrix, 1,3-bis(N-carbazolyl)benzene (mCP) as it has a suitably high triplet energy (E_T = 3.0 eV). The mCP matrix can also contribute to the suppression of non-radiative processes in the emitters, and host-guest interactions can also regulate triplet vibronic coupling and energies. We first studied the steady-state PL behavior of the two emitters in mCP at various doping concentrations (Figure S20). As doping concentration increases from 1 wt% to 10 wt%, there is only a 10 nm red-shift of the PL in PhCz-O-DiKTa, while in PhCz-DiKTa there is a slightly larger 20 nm spectral red-shift. This study reveals that there is very little aggregation at these doping concentrations as suggested by the absence of strong intermolecular interactions in the crystal structures. A remarkable enhancement in the ΦPL values of 80% and 91% for PhCz-O-DiKTa and PhCz-DiKTa in N2, respectively, was recorded at 10 wt%
doping compared to those at 1 wt% ($\Phi_{PL} < 55\%$) and 5 wt% ($\Phi_{PL} < 70\%$) doping (Table S5). Thus, 10 wt% emitter-doped mCP films were selected for further photophysical measurements. The corresponding photophysical data are summarized in Tables S6 and S7. Similar spectral profiles of the steady-state (SSPL), prompt, and delayed emissions were recorded in PhCz-O-DikTa and PhCz-DiKTa, with the SSPL maxima, $\lambda_{PL}$, of ~500 nm and ~525 nm (Figures 5a and 5b), respectively; the FWHMs of PhCz-O-DikTa and PhCz-DiKTa are 57 nm and 72 nm, respectively. The spectral FWHM broadening probably results from the enhanced electronic coupling from interactions of dimeric species in addition to host-guest interactions compared to the emission of isolated monomers (Figure 3b). Multiexponential decay kinetics were observed, with prompt fluorescence lifetimes, $\tau_P$, for PhCz-O-DikTa and PhCz-DiKTa of 8.0 ns and 10.1 ns (Figure S21), respectively, and delayed fluorescence lifetimes, $\tau_{DF}$, of 653.5 $\mu$s and 103.8 $\mu$s in vacuum (Figure 5d), respectively. Temperature-dependent transient PL decay behavior revealed that both compounds are TADF emitters (Figure S22).

The recorded $\Phi_{PL}$ values of PhCz-O-DikTa and PhCz-DiKTa in air are 56% and 73% (Table S6), respectively, which improve to 80% and 91% in N$_2$, respectively. Based on the contribution of the delayed component to the average $\tau_{DF}$, the calculated $\Phi_{DF}$ associated with the delayed fluorescence in N$_2$ are 59% and 78% for PhCz-O-DikTa and PhCz-DiKTa, respectively (Figure 5e). The $\Delta E_{S\text{T}1T1}$ values estimated from the difference in energy between the onsets of the prompt fluorescence and delayed emission are almost identical (0.18 eV vs 0.19 eV) (Figures 5c and 5f). However, the calculated $k_{RISC}$ values of PhCz-O-DikTa and PhCz-DiKTa are $5.44 \times 10^3$ s$^{-1}$ and $6.64 \times 10^4$ s$^{-1}$ (Table S7), respectively, representing a 12-fold enhancement in the latter despite the similar $\Delta E_{S\text{T}1T1}$. However, according to Marcus electron transfer theory, the $k_{RISC}$ of PhCz-DiKTa should be slower than that of PhCz-O-DikTa because the SOC constant of PhCz-DiKTa between $S_1$ and $T_1$ states is much smaller than that of PhCz-O-DikTa (0.10 cm$^{-1}$ vs 0.43 cm$^{-1}$, Figure S14a). Thus, a higher-lying triplet excited state $T_2$ probably serves as a bridge for boosting the spin vibronic coupling via second-order perturbation.
**Figure 6.** Temperature-dependent (a, b) steady-state and (c, d) time-gated PL spectra of (a, c) 10 wt% PhCz-O-DiKTa and (b, d) 10 wt% PhCz-DiKTa in mCP in vacuum. Time-gated window: 1-10 ms for PhCz-O-DiKTa and 0.2-2 ms for PhCz-DiKTa; λ_{exc} = 350 nm; inset: photos showing variable afterglows at 200 K and 77 K, excited by 365 nm UV torch.

Temperature-dependent PL measurements were further performed to evidence the presence of the T₂ state. As temperature decreases from 298 K to 200 K, the λ_{PL} of the steady-state PL spectrum of PhCz-O-DiKTa gradually red-shifts from 504 nm to 512 nm (Figure 6a), together with a remarkable enhancement in emission intensity. This excludes TADF as the origin for this spectral change as the intensity should weaken with decreasing temperature if the origin were TADF. Thus, this highly strengthened PL must originate from emission from triplet excitons. As the temperature further decreases to 77 K, the emission intensity at 512 nm diminishes accordingly, and a new concomitant T₁ emission at 540 nm emerges. Evidently, the intensity ratio between 540 nm and 512 nm increases due to the suppressed thermal activation of excitons from T₁ to T₂ states (Figure 6a). The picture of PhCz-DiKTa is similar as a function of temperature (Figure 6b). Next, temperature-dependent time-gated measurements were conducted to isolate the T₁ and T₂ emissions. As the temperature decreases to 200 K, compared to the TADF emission at ~500 nm, the enhanced T₂ phosphorescence centered at 515 nm appears (as a result of the combined suppressed RISC and nonradiative transitions), and then gradually disappears. Alongside this, there is the emergence and enhancement of T₁ phosphorescence.
at 550 nm as temperature decreases to 77 K, which cuts off thermally activated reverse internal conversion. \(T_1\) and \(T_2\) phosphorescence can also be evidenced by green and yellow phosphorescence afterglows at 200 K and 77 K (Figure 6c, inset), respectively. Notably, the \(T_2\) emission recorded in mCP is blue-shifted compared to \(T_1\) recorded in 2-MeTHF glass at 77 K, which removes the possibility that \(T_2\) phosphorescence originates from emission from low-energy aggregates (Figure S23). A similar phosphorescence evolution over temperature can be observed in PhCz-DiKTa (Figure 6d). At 200 K, there is a strongly enhanced \(T_2\) phosphorescence at 534 nm, while at 77 K \(T_1\) phosphorescence dominates the time-gated PL spectrum. Similarly, two different phosphorescence afterglows were observed at 200 K and 77 K (Figure 6d, inset). Normalized phosphorescence spectra of PhCz-DiKTa and PhCz-O-DiKTa gradually red-shift with decreasing temperature, reflecting the varying contributions from emissive \(T_2\) and \(T_1\) states (Figure S24). The increasing phosphorescence lifetimes measured at 515 nm and 550 nm as temperature decreases are consistent with the presence of emissive \(T_2\) and \(T_1\) states (Figures S25 and S26). The \(T_2\) energies, estimated from the onsets of the phosphorescence spectra of PhCz-O-DiKTa and PhCz-DiKTa at 200 K, are 2.54 eV and 2.51 eV (Figure S27), respectively; thus, the estimated \(\Delta E_{S1T2}\) values are 0.11 eV and 0.07 eV, respectively, which are close to predicted \(\Delta E_{S1T2}\) values shown in Figure 2b. The smaller \(\Delta E_{S1T2}\) of PhCz-DiKTa correlates with the recorded shorter \(\tau_d\) and faster \(k_{RISC}\) compared to those of PhCz-DiKTa (Figure 5c and Table S7).

**OLED performance**

The thermally evaporated bottom-emitting devices with PhCz-O-DiKTa and PhCz-DiKTa were next fabricated using a device structure of ITO/HATCN (5 nm) /TAPC (40 nm)/TCTA (10 nm)/10 wt% emitter in mCP (20 nm)/TmPyPB (50 nm)/LiF (0.7 nm)/Al (100 nm) (Figure 7a), where ITO (indium tin oxide) serves as the transparent anode, HATCN (1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile) acts as the hole-injection layer, TAPC (1,1-bis[(di-4-tolylamino)phenyl]cyclohexane) act as the hole-transporting layer, TCTA act as the electron blocking layer, mCP is the host, TmPyPB (1,3,5-tris(3-pyridyl-3-phenyl)benzene) acts both as an electron transporting layer and a hole blocking layer and LiF (lithium fluoride) acts as an electron-injection layer by modifying the work function of aluminum (Al) cathode. The molecular structures of these materials are presented in Figure 7b. Although we have demonstrated that a high doping concentration leads to emission broadening (Figure S20), the 10 wt% emitter doping concentration was chosen due to the recorded high \(\Phi_{PL}\) values. The EL data are summarized in Table 1.
Figure 7. (a) Device configuration with energy levels and thickness for each layer. (b) Molecular structures of materials employed in the devices. (c) EL spectra. (d) Simplified Jablonski diagram showing the hole–electron recombination process under electrical excitation; RIC: reverse internal conversion. (e) Current-voltage-luminance characteristic. (f) EQE as a function of luminance; inset: photos of electroluminescence from the devices.

Table 1. Summary of OLED performance.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>$\lambda_{\text{EL}}$</th>
<th>FWHM</th>
<th>CIE $\text{a}$</th>
<th>$V_{\text{on}}$</th>
<th>$\text{CE}_{\text{max}}$</th>
<th>$\text{PE}_{\text{max}}$</th>
<th>EQE $\text{e}$</th>
<th>$L_{\text{max}}$</th>
</tr>
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<tr>
<td>PhCz-O-DiKTa</td>
<td>497</td>
<td>58</td>
<td>0.21, 0.55</td>
<td>3.0</td>
<td>56.0</td>
<td>58.6</td>
<td>20.0/9.1/1.9</td>
<td>22052</td>
</tr>
<tr>
<td>PhCz-DiKTa</td>
<td>524</td>
<td>72</td>
<td>0.31, 0.61</td>
<td>2.8</td>
<td>76.3</td>
<td>85.6</td>
<td>22.0/19.0/11.1</td>
<td>48322</td>
</tr>
</tbody>
</table>

$a$ EL maximum, FWHM and CIE coordinates recorded at 4 V. $b$ Turn-on voltage at EQE$_{\text{max}}$. $c$ Maximum current efficiency. $d$ Maximum power efficiency. $e$ Maximum EQE/EQE at 100 cd m$^{-2}$/EQE at 1000 cd m$^{-2}$. $f$ Maximum luminance at 7.6 V.

Shown in Figure 7c are the EL spectra of the two devices. EL maxima ($\lambda_{\text{EL}}$) of the devices with PhCz-O-DiKTa and PhCz-DiKTa are 497 nm and 524 nm and associated FWHM of 58 nm and 72 nm, respectively. The corresponding Commission Internationale de l’Éclairage (CIE) coordinates are
energies of the T-dependent steady and leading OLEDs by judiciously decorating the core emitter with a PhCz group. This serves to reduce the $\Delta E_{S1T2}$, leading to an accelerated RISC. Theoretical modelling of two MR-TADF emitters, PhCz-O-DiKTa and PhCz-DiKTa, predicts that the T$_2$ state could act as a conduit in boosting $k_{RISC}$. Temperature-dependent steady-state and time-gated PL measurements provided evidence of the presence and energies of the T$_2$ state, which explains why PhCz-DiKTa possesses a near 12-fold enhancement in $k_{RISC}$ compared to PhCz-O-DiKTa. The OLED devices with PhCz-O-DiKTa and PhCz-DiKTa show relatively low turn-on voltages ($V_{on}$) of ~3.0 eV at maximum EQE. The obtained high maximum luminance ($L_{max}$) of over 22,000 cd m$^{-2}$, benefitting from the suitable energy cascade between the functional layers (Figure 7c). Given that the measured $\Phi_{PL}$ value of PhCz-O-DiKTa and PhCz-DiKTa are 80% and 91%, respectively, the theoretical maximum external quantum efficiency (EQE$_{max}$) values are 20% and 22.75%, assuming an out-coupling efficiency of 25%. As depicted in Figure 7f, the EQE$_{max}$ values of the devices with PhCz-O-DiKTa and PhCz-DiKTa are 20.0% and 22.0%, reflecting that both devices reach a near 100% exciton utilization efficiency with the maximum current efficiency (CE$_{max}$) and power efficiency (PE$_{max}$) values are 56.0 cd A$^{-1}$ and 58.6 lm W$^{-1}$ of PhCz-O-DiKTa and 76.3 cd A$^{-1}$ and 85.6 lm W$^{-1}$ of PhCz-DiKTa devices (Figure S29). However, the efficiency roll-off behaviour diverges between the two devices. At a luminance of 100 cd m$^2$, a large efficiency roll-off of 54.5% is observed in the device with PhCz-O-DiKTa, which is ameliorated considerably to 13.6% in the device with PhCz-DiKTa. The EQE reduces to 2.9% at a luminance of 1000 cd m$^2$ for the device with PhCz-O-DiKTa; however, for the device with PhCz-DiKTa, the EQE$_{1000}$ remains at 11.1%. A plausible explanation for this difference is that the smaller $\Delta E_{S1T2}$ in PhCz-DiKTa serves to mitigate the efficiency roll-off due to the faster $k_{RISC}$ and shorter delayed lifetime, thus reducing triplet exciton populations at high current densities. However, most of the previously reported ketone-based MR-TADF OLEDs showed rather severe efficiency roll-off ($>45\%$)[21-26,43,44] the origin of the large roll-off has not been explored in any detail. A summary of previously reported EL data related to ketone-based MR-TADF devices is presented in Figure S30. This report experimentally demonstrates that the T$_2$ state is the key to regulating $k_{RISC}$ (Figure 7d) and provides insight into improving the efficiency roll-off of devices, at least with ketone-containing MR-TADF derivatives.

**Conclusions**

In summary, we demonstrate how it is possible to dramatically reduce efficiency roll-off in MR-TADF OLEDs by judiciously decorating the core emitter with a PhCz group. This serves to reduce the $\Delta E_{S1T2}$, leading to an accelerated RISC. Theoretical modelling of two MR-TADF emitters, PhCz-O-DiKTa and PhCz-DiKTa, predicts that the T$_2$ state could act as a conduit in boosting $k_{RISC}$. Temperature-dependent steady-state and time-gated PL measurements provided evidence of the presence and energies of the T$_2$ state, which explains why PhCz-DiKTa possesses a near 12-fold enhancement in $k_{RISC}$ compared to PhCz-O-DiKTa. The OLED devices with PhCz-O-DiKTa and PhCz-DiKTa.
exhibited EQE\textsubscript{max} values of 20.0\% and 22.0\%, respectively, indicating 100\% exciton. The remarkable divergence in efficiency roll-off of the two devices was ascribed to the smaller $\Delta E_{\text{STT}}$ in the device with PhCz-DiKTa. This study provides a rarely documented yet clear picture of the dynamics of intermediate triplet excited states and a possible solution to improve device performance without sacrificing color purity.

Notes

There is no interest conflict to declare.

Supporting Information

$^1$H and $^{13}$C NMR spectra, HRMS, HPLC, EA of the target compounds, and supplementary computational and photophysical data have been presented in the supporting information. Crystallographic data for CCDC 2219898-2219899 contains the supplementary crystallographic data for PhCz-O-DiKTa and PhCz-DiKTa. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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References


