Improving Processability and Efficiency of Resonant TADF Emitters: A Design Strategy

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A new design strategy is introduced to address a persistent weakness with resonance thermally activated delayed fluorescence (R-TADF) emitters to reduce aggregation-caused quenching effects, which are identified as one of the key limiting factors. The emitter Mes$_3$DiKTa shows an improved photoluminescence quantum yield of 80% compared to 75% for the reference DiKTa in 3.5 wt% 1,3-bis(N-carbazolyl)benzene. Importantly, emission from aggregates, even at high doping concentrations, is eliminated and aggregation-caused quenching is strongly curtailed. For both molecules, triplets are almost quantitatively upconverted into singlets in electroluminescence, despite a significant ($\approx 0.21$ eV) singlet-triplet energy gap ($\Delta E_{ST}$), in line with correlated quantum-chemical calculations, and a slow reverse intersystem crossing. It is speculated that the lattice stiffness responsible for the narrow fluorescence and phosphorescence emission spectra also protects the triplets against nonradiative decay. An improved maximum external quantum efficiencies (EQE$_{max}$) of 21.1% for Mes$_3$DIKTa compared to the parent DiKTa (14.7%) and, importantly, reduced efficiency roll-off compared to literature resonance TADF organic light-emitting diodes (OLEDs), shows the promise of this design strategy for future design of R-TADF emitters for OLED applications.

1. Introduction

Thermally activated delayed fluorescence (TADF) permits 100% internal quantum efficiency (IQE) in electroluminescent devices as this mechanism permits conversion of nonradiative triplet excited states to radiative singlet states via reverse intersystem crossing (RISC).[1] RISC is made efficient by having a small energy gap between the lowest triplet and singlet excited states ($\Delta E_{ST}$). The most common molecular design for achieving small $\Delta E_{ST}$ in organic emitters is based on a donor–acceptor paradigm where the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are poorly electronically coupled and usually spatially separated, thus reducing the exchange integral.[2] Conventional donor–acceptor TADF compounds emit from an excited state that is strongly charge transfer (CT) in nature. Generally, these CT emitters have emission spectra that are...
very broad in nature, with full-width at half-maximum (FWHM), often as high as 100 nm, leading to poor color purity.[3]

In 2015, a new approach for TADF emitters was presented by Hatakeyama and co-workers.[4] Their design involved an alternating HOMO/LUMO pattern based on complimentary resonance effects of electron-donating oxygen and electron-withdrawing boron moieties (Figure 1a). The first emitter of this resonating TADF (R-TADF) family, DABOA (originally called 2a, but renamed for clarity), possessed a suitably small $\Delta E_{ST}$ of 0.15 eV and a reasonably high photoluminescence quantum yield, $\Phi_{PL}$, of 72% in 1 wt% poly(methyl methacrylate) (PMMA) thin film. In this first report no devices were fabricated as the emission maximum, $\lambda_{PL}$, was too high in energy at 399 nm.[4]

Following this initial work, the same group modified their design and incorporated stronger nitrogen-based donor moieties (Figure 1c).[5] Blue-emitting compounds DABNA-1 and DABNA-2 ($\lambda_{PL} = 460$ and 469 nm, respectively), showing very high $\Phi_{PL}$ of 88 and 90%, respectively, in 1 wt% mCBP, were reported. These emitters were incorporated into organic light-emitting diodes (OLEDs), which showed very good maximum external quantum efficiencies ($\text{EQE}_{\text{max}}$) of 13.2% and 20.2%, respectively. Though the OLEDs showed very large efficiency roll-off and did not reach a luminance of 1000 cd m$^{-2}$, DABNA-2 nevertheless represents one of the most efficient deep blue emitters reported to date with Commission Internationale d’Eclairage (CIE) coordinates of (0.12, 0.13).[6]

Building from DABNA-1, the C$_3$-symmetric derivative TABNA (originally named 2, renamed for clarity) likewise showed a similarly small $\Delta E_{ST}$ of 0.21 eV along with a reasonable $\Phi_{PL}$ of 54% in 1 wt% PMMA films; however, the undesired blueshift in the emission ($\lambda_{PL} = 399$ nm) again led to no devices being fabricated.[7] Going beyond the simplistic orbital picture, we demonstrated, based on highly correlated quantum chemical calculations at the spin-component scaling second-order approximate coupled-cluster (SCS-CC2) level of theory, that DABNA-1 and TABNA display short-range charge transfer in both the $T_1$ and $S_1$ excited states, which is responsible for their small $\Delta E_{ST}$ while maintaining the necessary overlap between

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**Figure 1.** Previously reported R-TADF emitters. a) Simplified resonating HOMO/LUMO plot for DABOA and HOMO-LUMO distributions calculated using density functional theory (DFT); b) simplified difference density plot of DABOA and singlet and triplet difference density plots calculated in the gas phase using spin-component scaling second-order approximate coupled-cluster (SCS-CC2) approach; c) structures of previously reported R-TADF emitters and related photophysical and OLED data.
the hole and electron wavefunctions to guarantee a large oscillator strength, $f$, which explains their high observed $\Phi_{PL}$.\[3\]

Increasing the number of acceptor groups (B2, B3, and B4) stabilized the LUMO energy and led to blueshifted emission with emission maxima, $\lambda_{PL}$, of 455, 441, and 450 nm, respectively, in 1 wt% PMMA.\[8\] Further, an excellent device performance using B2, was reported with $\text{EQE}_{\text{max}}$ values as high as 18%, coupled with a slightly improved efficiency roll-off compared to the devices with the DABNA emitters. The next iteration in design involved the introduction of a donor carbazole derivative and solubilizing tert-butyl groups about the skeleton of DABNA-1 (TBN-TPA).\[9\] The addition of the tert-butylcarbazole unit did not adversely affect the multiresonance mechanism, with HOMO/LUMO density remaining localized on the DABNA-1 core and only a slight observed redshift in the emission at 470 nm ($\lambda_{PL}$ of DABNA-1 = 460 nm) coupled with an enhanced $\Phi_{PL}$ of 98% in toluene ($\Phi_{PL}$ of DABNA-1 = 89% in CH$_2$Cl$_2$). The OLED using TBN-TPA showed an excellent $\text{EQE}_{\text{max}}$ of 32.1% and also an improved efficiency roll-off.\[9\] Another method to improve efficiency roll-off has been proposed recently where a tert-butyl analogue of DABNA-1, t-DABNA ($\lambda_{PL}$ = 445), was used alongside an assistant TADF dopant DMAC-DPS.\[10\] Improved $\text{EQE}_{\text{max}}$ values from 25.1% to 31.4% were observed in the assistant dopant device compared to the OLED with no assistant dopant. Vastly improved efficiency roll-off was also observed where the EQE at 100 cd m$^{-2}$ decreased by only 13% in the assistant dopant device compared to 76% in the device without the assistant dopant. Hatakeyama and co-workers\[11\] recently reported a B/N containing pentacene decorated with peripheral diphenylamines (v-DABNA). The deep blue devices reported show outstanding $\text{EQE}_{\text{max}}$ and very low efficiency roll-off at 100 cd m$^{-2}$ of 34.4% and 5% ($\text{EQE}_{100} = 32.8\%$), respectively, at CIE of (0.12,0.11). To the best of our knowledge, these OLEDs are the highest performing deep-blue devices reported to date. The OLEDs also show very high color purity, with a FWHM of 18 nm in a 1 wt% doped device. A summary of all major photophysical data of literature B/N R-TADF based emitters is in Table S1 (Supporting Information).

R-TADF emitters are clearly very promising, with $\text{EQE}_{\text{max}}$ of up to 30% possible for blue devices, but their most attractive feature is their consistently narrow emission FWHM. The sharper emission profile is particularly attractive as this translates to improved color purity in the device.\[12\] R-TADF compounds have small $\Delta E_{ST}$, high $\Phi_{PL}$, and small emission FWHM, making them an ideal class of emitter for OLEDs. However, as many of the examples in Figure 1c are highly planar, they are at risk of quenching due to aggregation and/or excimer formation. Further, nearly all are based on a B/N design, which limits the structural diversity and scope of these emitters.

Mes$_3$DiKTa (Figure 2) was designed in order to mitigate the undesirable quenching by aggregation frequently observed in R-TADF emitters. The mesityl groups were chosen as they would (1) adopt an orthogonal conformation and thus not affect the multiresonance mechanism and (2) their steric bulk will inhibit aggregation-caused quenching.\[13\] DiKTa, acting as a reference emitter, and derivatives have been previously reported; however, their potential as TADF emitters was...
not identified until very recently, being initially categorized as normal fluorescent emitters. Since commencing our study, DiKTa has been reported as a R-TADF emitter under the name of QAO. [15] It has a high \( \Phi_{\text{PL}} \) of 72% and narrow blue emission (\( \lambda_{\text{PL}} = 486 \) nm; FWHM = 39 nm) in 5 wt% 1,3-bis(N-carbazolyl) benzene (mCP), and a high \( \Phi_{\text{EQE}} \) of 19.4% (at <1 cd m\(^{-2}\)). However, the maximum luminance was only 1100 cd m\(^{-2}\) and only limited theoretical work was performed. A second emitter in the same report, QAO-DAd, is much better described as a donor–acceptor system and showed none of the photophysical characteristics emblematic of R-TADF emitters. In addition, two phenyl substituted derivatives of DiKTa were reported, 3-PhQAD and 7-PhQAD.[16] Near identical \( \lambda_{\text{PL}} \) to DiKTa were reported at 466 and 464 nm in 2 wt% mCP, respectively, for 3-PhQAD and 7-PhQAD along with comparable \( \Phi_{\text{PL}} \) of 73% and 68%. Addition of the phenyl groups has very little impact upon the photophysics of the DiKTa luminophore nor on the device performance where comparable \( \Phi_{\text{EQE}} \) of 19.1% and 18.7% were reported for 3-PhQAD and 7-PhQAD, respectively. The OLED with 7-PhQAD showed a significant efficiency roll-off with \( \Phi_{\text{EQE}} \) of 5.4% compared to 10.2% for 3-PhQAD; however, no explanation was given for this observation. Further, a drop-in luminance compared to the best boron-based R-TADF emitters was observed for 3-PhQAD (4975 cd m\(^{-2}\)) and 7-PhQAD (2944 cd m\(^{-2}\)). There is thus a clear need for improvement in the performance of this new class of R-TADF emitter. Using in silico design and building from our previous work, we demonstrate that peripheral modification of a R-TADF triangulene-type emitter does not affect the R-TADF mechanism, and reduces quenching by aggregation. Mes\(_3\)DiKTa shows an enhanced \( \Phi_{\text{PL}} \) of 80% compared to 75% for the reference DiKTa at 3.5 wt% in mCP. An excellent \( \Phi_{\text{EQE}} \) of 21.1% at a luminance of 25 cd m\(^{-2}\) was obtained, representing the highest for these ketone-based R-TADF emitters. Importantly, improved efficiency roll-off of 31% was also noted with \( \Phi_{\text{EQE}} \) of 14.5% and a significantly higher maximum luminance of 12 900 cd m\(^{-2}\) for the OLED with Mes\(_3\)DiKTa.

2. Results and Discussion

2.1. Computational Studies

Based on our recent study,[3] all the results presented in the main manuscript are obtained by running higher-level SCS-CC2: for completeness, time-dependency density functional theory (TD-DFT) calculations are presented in Figure S32 (Supporting Information). All TD-DFT flavors (namely, different functionals and full TD-DFT versus Tamm-Dancoff approximation treatment) lead to different description of both \( T_1 \) and \( S_1 \) excited states in comparison to SCS-CC2, and also to large overestimations of \( \Delta E_{\text{ST}} \). Similar to results obtained for DABNA-1 and TABNA, including high-order electronic correlation effects is required to properly account for the short-range charge transfer character in the lowest singlet and triplet excited states of both DiKTa and Mes\(_3\)DiKTa, revealing that the R-TADF mechanism is operative. As expected, there is very little density located on the mesityl groups in Mes\(_3\)DiKTa (Figure 2). However, the difference density plots show opposite patterns to the previously reported B,N R-TADF emitters because of the inverted design which places a central nitrogen-based donor and peripheral ketone acceptors. In order to further validate our computational methodology and demonstrate its robustness, calculations were performed for each of the literature R-TADF diketone emitters in Figure 1, along with other B,N R-TADF emitters, namely, DABNA-2, t-DABNA, and TBN-TPN. Predicted \( \Delta E_{\text{ST}} \) energies are in good agreement with experiment (Table S9, Supporting Information). We note that our calculations on 3-PhQAD and 7-PhQAD sensibly disagree with the interpretation proposed by Zhang and co-workers[16] based on TD-DFT calculations, where the nature of the excited states in these compounds involves CT-LE hybridization, while our SCS-CC2 calculations suggest that \( T_1 \) and \( S_1 \) are short-range CT excited states.

Calculated \( \Delta E_{\text{ST}} \) for DiKTa and Mes\(_3\)DiKTa are 0.27 and 0.26 eV, respectively, and are expected to be small enough to permit RISC at ambient temperatures. Predicted oscillator strengths, \( f \), of 0.20 and 0.23 for each DiKTa and Mes\(_3\)DiKTa, respectively, resulting in \( k_e \) of \( 1.05 \times 10^8 \) and \( 1.10 \times 10^8 \) s\(^{-1}\) from \( S_1 \) to \( S_0 \), which should translate into enhanced \( \Phi_{\text{PL}} \).

2.2. Synthesis

DiKTa was synthesized using a similar method to that reported previously (Figure 2).[3] Diester, 1 was obtained in modest yield of 32% via a high-temperature Ullmann coupling. The subsequent ring closing reaction produced DiKTa in 86% yield. Overall a reduced yield of 26% compared to the original 31% was obtained.[14a] Mes\(_3\)DiKTa was obtained in good yield following bromination of intermediate 2, Friedel-Craft acylation to produce brominated Br\(_3\)DiKTa, and Suzuki-Miyaura coupling with mesityl-2-boronic acid to deliver the target Mes\(_3\)DiKTa. \(^1\)H and \(^13\)C NMR, high resolution mass spectrometry, elemental analysis, and high-performance liquid chromatography were used to confirm the structures along with the purity. Single crystal X-ray diffraction data for both emitters indicated different packing motifs; although neither compound shows strong intermolecular interactions, the presence of the mesityl groups does disrupt \( \pi \cdot \cdot \cdot \pi \) interactions in Mes\(_3\)DiKTa [no centroid- centroid distances less than 4.030(3) Å]. The only intermolecular interactions seen in Mes\(_3\)DiKTa are extremely weak C–H · · · π interactions between a phenyl hydrogen and a mesitylene ring, at distances close to the van der Waals limit (2.85 and 2.06 Å), leading to the formation of weakly interacting molecular stacks along the crystallographic \( b \)-axis. In DiKTa \( \pi \cdot \cdot \cdot \pi \) interactions are found [centroid- centroid distance of 3.8793(6) Å] between adjacent emitter molecules, giving rise to interacting stacks running along the \( c \)-axis (Figure S17, Supporting Information). Good thermal stability was observed with 5% weight loss at 323 and 437 °C for DiKTa and Mes\(_3\)DiKTa, respectively (Figure S29, Supporting Information).

2.3. Optoelectronic Properties

The electrochemical behavior of DiKTa and Mes\(_3\)DiKTa was studied by cyclic voltammetry and differential pulse
voltammetry in degassed acetonitrile (MeCN) with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) are shown in Figure 3a and the data are summarized in Table S3 (Supporting Information). A slightly destabilized HOMO and stabilized LUMO in Mes3DiKTa versus DiKTa can be attributed to the mesomeric electron-withdrawing character of the mesityl groups. The reduced ΔE_H-L in turn is correlated with the observed redshifted emission (vide infra). Further, the mesityl groups contribute to the electrochemical stability of the compound with reversible oxidation and reduction waves by inhibiting an electrochemical degradation process located at the para-C–H position to the nitrogen. Atmospheric photoelectron spectroscopy (APS) was also performed on neat films of the emitters to corroborate the HOMO levels inferred from CV (Figure S18, Supporting Information). The APS values are in good agreement with those obtained by DPV (Table S3, Supporting Information). UV–vis spectra in toluene show high-energy, low-intensity bands along with a low-energy high-intensity band, the latter of which we attribute to a short-range charge-transfer S0–S1 strongly allowed optical transition typical of multiresonant compounds (Figure 3b and Figure S19, Supporting Information). This is in good agreement with theory, where a high oscillator strength, f, of 0.23 and 0.20 for Mes3DiKTa and DiKTa is predicted for this transition. A very small positive solvatachromism is observed for this band in the ground state (Figure S19, Supporting Information). This is again consistent with the short-range CT nature of this transition (cf. Tables S4 and S5, Supporting Information).

We next investigated the photophysical properties of the two emitters in toluene. The photoluminescence (PL) spectrum of Mes3DiKTa shows the expected mirror image profile to the absorption spectrum, and the small difference between the peaks of the absorption and emission of 27 nm (805 cm⁻¹) suggests a weak geometry relaxation in the singlet state (Figure 3c and Figure S20a, Supporting Information, for DiKTa) highlighting the quite rigid structure of Mes3DiKTa similarly to

Figure 3. Solution optoelectronic properties. a) Cyclic and differential pulse voltammograms in degassed MeCN with 0.1 M [nBu4N]PF6 as the supporting electrolyte and Fc/Fc' as the internal reference (0.38 V vs SCE).[17] b) Absorption (Abs) and steady-state PL (SS) spectra obtained in toluene at 300 and 77 K, phosphorescence (Phos.) spectra obtained in toluene glass at 77 K after 70 ms delay for 70 ms, λex = 415 nm. c) solvatochromatic PL study of Mes3DiKTa, λex = 345 nm. d) Time resolved PL of Mes3DiKTa and DiKTa in degassed toluene, λex = 355 nm detected across the full spectral range, where IRF is the instrument response function.
DABNA-1: the vibronic progression is less well resolved in the PL spectrum. The rigid nature of the compound is responsible for the narrow emission spectrum at RT. A similar profile but with more pronounced vibronic progression is observed for the phosphorescence spectrum obtained after 70 ms at 77 K in a toluene glass. The $\Delta E_{ST}$ of 0.19 eV is sufficiently small to enable a RISC process at room temperature. Modest positive solvatochromism (31 nm, or 1522 cm$^{-1}$) for DiKTa and 1408 cm$^{-1}$ for Mes$_3$DiKTa was observed in the steady-state PL spectra (Figure 3c), in contrast to the larger positive solvatochromism shown in Solution photophysical data for both emitters in toluene are their transition dipole moment compared to the gas phase.

Table of 3.5 wt% emitter in mCP (found in Tables S4–S6, Supporting Information). This same behavior is observed for DiKTa (Figures S22–S24, Supporting Information). Much like that observed in toluene, the contribution of the delayed emission to the overall emission in DiKTa is more prominent than for Mes$_3$DiKTa (Figure S25, Supporting Information), indicating higher TADF emission contribution, possibly associated with the smaller $\Delta E_{ST}$ in DiKTa.

Figure 4c shows the spectral analysis of the prompt fluorescence at 77 K and phosphorescence (time delay 20 ms) at 77 K for Mes$_3$DiKTa in 3.5 wt% mCP (see Figure S24a, Supporting Information, for DiKTa). We were able to estimate the $\Delta E_{ST}$ from the onset of these spectra. The slight redshifted emission observed in Mes$_3$DiKTa, for both the $S_1$ and $T_1$ states (Table 3) versus DiKTa can be correlated to the observed smaller electrochemical gap. Good agreement for $\Delta E_{ST}$ between experiment and theory is observed, with DiKTa ($\Delta E_{ST}\text{exp} = 0.20$ eV vs $\Delta E_{ST}\text{theory} = 0.27$ eV), while for Mes$_3$DiKTa the $\Delta E_{ST}$ was found to be 0.21 eV and computed to be 0.26 eV.

2.4. Organic Light-Emitting Diodes

To evaluate the potential of DiKTa and Mes$_3$DiKTa in devices we fabricated several OLEDs, the two devices presented here are representative of the OLEDs tested (more device results are shown in Figures S27 and S28, Supporting Information). The device architecture was challenging as both emitters possess very deep HOMO levels. Thus, the difficulty to design these OLEDs arises from the very limited number of hosts with suitably deep HOMO levels.

Table 1. Solution lifetime data, rates, and efficiencies for DiKTa and Mes$_3$DiKTa in degassed dilute toluene at 300 K.

| Compound   | $\lambda_{exc}$ [nm] | FWHM$^a$ [nm] | (cm$^{-1}$) | $\Phi_{PL}$ ($\Phi_{DI}$)$^b$ [%] | $\tau_{PL}$ $\tau_{DC}$ [ns]; µs | $k_d/10^5$ s$^{-1}$ | $k_c/10^8$ s$^{-1}$ | $\Phi_{SC}$ [%] | $\kappa_{ISC}/10^4$ s$^{-1}$ |
|------------|----------------------|----------------|----------|----------------------------------|---------------------------------|---------------------|------------------|-------------|---------------------|
| DiKTa      | 453$^a)$              | 27 (1251)$^a)$ | 26 (1)   | 5.1; 23                          | 4.9                             | 14                  | 0.75             | 3.8         | 2.7                 |
| Mes$_3$DiKTa | 468$^a)$             | 29 (1306)$^a)$ | 37 (1)   | 6.7; 33                          | 5.4                             | 9.1                 | 0.4              | 2.7         | 3.1                 |

$^a$In degassed toluene; $^b\lambda_{exc} = 360$ nm; $^c\lambda_{exc} = 355$ nm, prompt and delayed fluorescence were fitted as single exponential decays, shown in Figure S26 (Supporting Information). $^d\lambda_{exc} = 335$ nm; $\lambda_{exc} = 345$ nm.
function of the aluminum cathode. The doping ratio was optimized at 3.5 wt% for both emitters as a function of $\Phi_{PL}$ and to avoid broadening FWHM due to aggregation formation as observed in Mes$_3$DiKTa devices with doping ratio ranging from 3.5% to 30% (Figure S28b, Supporting Information).

Both electroluminescence (EL) spectra are very narrow with FWHM of 39 and 36 nm (1848 and 1572 cm$^{-1}$), and associated CIE chromaticity coordinates of (0.14, 0.18) and (0.12, 0.32) for DiKTa and Mes$_3$DiKTa, respectively (Figure 5b).

These EL spectra are significantly narrower than conventional blue D-A TADF OLEDs but similar to those EL spectra observed in R-TADF emitters (Table S5, Supporting Information). The EL spectra of our devices also showed very weak emission from the host at high voltages that likely occurs due to the slightly shallower HOMO level of mCP than the emitters (Figures S27a and S28a, Supporting Information).

Figure 5d shows EQE versus luminance curves. The DiKTa OLED shows an EQE$_{max}$ of 14.7% at 8 cd m$^{-2}$ while the OLED

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### Table 2. Thin film photophysical data at 3.5 wt% in mCP.

| Compound   | $\lambda_{PL}$ [nm] | FWHM [nm] (cm$^{-1}$) | $\Phi_{PL}$ [%] | $\tau_p$, $\tau_d$ [ns]; $\mu$ | $T_1$ [eV] | $S_1$ [eV] | $\Delta E_{ST}$ [eV] |
|------------|----------------------|------------------------|-----------------|-----------------|-------------|-------------|------------------|
| DiKTa      | 463$^e$              | 37 (1824)              | 75$^i$          | 4.4, 15         | 2.55        | 2.75        | 0.20             |
| Mes$_3$DiKTa | 477                 | 37 (1689)              | 80              | 5.9, 20         | 2.46        | 2.67        | 0.21             |

$^a$$\lambda_{exc}$ = 355 nm at 300 K under vacuum, prompt component obtained using a single exponential, delayed obtained using a stretched exponential; $^b$Obtained from the onset of the PL spectrum at 77 K after 70 ms, $\lambda_{exc}$ = 415 nm; $^c$Obtained from the onset of the steady-state spectrum at 77 K, $\lambda_{exc}$ = 335 nm; $^d$$\Delta E_{ST} = E(S_1) - E(T_1)$; $^e$Obtained at 300 K, $\lambda_{exc}$ = 335 nm; $^f$Calculated using an integrating sphere, under N$_2$, $\lambda_{exc}$ = 335 nm.

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**Figure 4.** Solid-state effects of spin-coated films. a) Emission spectra at various concentrations at 300 K of DiKTa and Mes$_3$DiKTa. b) Varying PLQY at different concentrations DiKTa and Mes3DiKTa under N$_2$, $\lambda_{exc}$ = 335 nm. The dashed line is a guide to the eye, based on fitting an exponential decay function to the data. c) Steady-state PL spectra at 300 K, at 77 K, and phosphorescence spectra in 3.5 wt% mCP, phosphorescence obtained at 77 K at a delay of 20 ms for 70 ms, $\lambda_{exc}$ = 415 nm. d) Variable temperature time-resolved PL spectra, $\lambda_{exc}$ = 355 nm in 3.5 wt% mCP, where IRF is the instrument response function.
with Mes_3DiKTa shows an EQE_max of 21.1% at 25 cd m^{-2}. Given these EQE_max values, the high Φ_PL of 80% and 75% in mCP and considering charge balance as 100% and outcoupling efficiency as 25%, the theoretical EQE_max for DiKTa and Mes_3DiKTa are ≈18% and ≈20%, respectively.[21] Thus, we can infer that essentially 100% of the triplet excitons are being efficiently harvested and converted to singlet excitons via the TADF mechanism. Though we must be careful, as there is some uncertainty on the efficiency of charge recombination and light extraction, this is a remarkable and somewhat unexpected result in view of the very low RISC rate in these molecules (see Table 1). It thus appears that, provided the triplets are protected against nonradiative loss mechanisms, a reasonably small ΔE_ST value as found in DiKTa and Mes_3DiKTa is enough to quantitatively upconvert

Table 3. Device metrics for OLEDs employing DiKTa and Mes_3DiKTa and those of devices with similar literature emitters.

| Emitter     | V_{on}[a] [V] | EQE_{max}[b] [%] | Lum_{max}[c] [cd m^{-2}] | EQE_{100}[d] [%] | EQE_{1000}[d] [%] | CIE (x,y)[e] | FWHM[f] [nm] | λ_{EL}[g] [nm] | Ref.  |
|-------------|---------------|------------------|--------------------------|------------------|-------------------|---------------|---------------|----------------|-------|
| DiKTa       | ≈3            | 14.7% at 8 cd m^{-2} | 10 385                   | 8.3              | 3.3               | 0.14,0.18     | 39            | 465            | This work |
| Mes_3DiKTa  | ≈3            | 21.1% at 25 cd m^{-2} | 12 949                   | 14.5             | 4.5               | 0.12,0.32     | 36            | 480            | This work |
| QAD (aka DiKTa) | N/A          | 19.4 at 0.2 cd m^{-2} | 1100                    | 9.4              | 1.4               | 0.13,0.18     | 39            | 468            | [15]    |
| 3Ph-QAD     | N/A           | 19.1 at 0.2 cd m^{-2} | 4975                    | 10.4             | 3.1               | 0.13,0.32     | 44            | 480            | [16]    |
| 7Ph-QAD     | N/A           | 18.7 at 0.2 cd m^{-2} | 2944                    | 5.4              | 2.1               | 0.12,0.24     | 34            | 472            | [16]    |

[a]V_{on} = Turn-on voltage; [b]EQE = external quantum efficiency; [c]Lum = luminance; [d]Subscript 100 and 1000 refers to values taken at 100 cd m^{-2} and at 1000 cd m^{-2}, respectively; [e]CIE = Internationale de L’Éclairage coordinates; [f]FWHM = full width at half maximum; [g]EL = electroluminescence.

Figure 5. OLED data for DiKTa and Mes_3DiKTa. a) Device structure, b) electroluminescent spectra, c) current density versus voltage curves, and d) external quantum efficiencies (EQE) versus luminance.
all triplet excitations. We thus conclude that the weak coupling between the electronic excitations and the nuclei vibrations associated with the rigid backbone structure not only results in narrow spectral emission but also appears to slow down competitive nonradiative decay channels.

At 100 cd m$^{-2}$ the EQE$_{100}$ value for the OLED with DiKTa is 8.3%, decreasing 44% from its maximum value. The EQE$_{100}$ for the device with Mes$_3$DiKTa is 14.5%, showing an efficiency roll-off of 31%. At 1000 cd m$^{-2}$ the EQE$_{100}$ values decrease dramatically to 3.3% and 4.5% for DiKTa and Mes$_3$DiKTa, which is a decrease of 78% and 79% from their maximum values. This serious efficiency roll-off at high driving voltages was observed in other R-TADF emitters such as DABNA-1 and DABNA-2,[5] and recently was also observed by Zhang and co-workers,[12] where 3-PhQAD and 7-PhQAD EQE values drop more than 85% from their maximum value at 1000 cd m$^{-2}$. Thus, we contend that the increased steric bulk afforded by the mesityl groups reduces the efficiency roll-off of the OLEDs when compared to 3-PhQAD and 7-PhQAD. Zhang and co-workers have investigated the mechanisms responsible for this strong efficiency roll-off and concluded that both triplet-triplet annihilation (TTA) and singlet exciton–polaron annihilation (SPA) play significant roles in the efficiency roll-off. Due to the similarity of 3-PhQAD and 7-PhQAD with our emitters and the similarity of the device structures, the cause of our efficiency roll-off is likely to be SPA and TTA as well. Even though the EQE values are poor at high driving voltages, the luminance levels reached by both emitters are excellent (Lumax$^{-100}$ = 10 400 cd m$^{-2}$ and Lumax$_{\text{Mes}_3\text{DiKTa}}$ = 13 000 cd m$^{-2}$), which is not often observed in TADF-based devices, including R-TADF OLED. Both devices operate at similar current densities and show low turn-on voltages of around 3 V (Figure S7c, Supporting Information). The previously reported OLEDs with DiKTa[15] using a similar device structure to the one used in this study showed EQE$_{\text{max}}$ of 19.4% but at luminance lower than 1 cd m$^{-2}$. At comparable luminance of 10, 100, and 1000 cd m$^{-2}$ they obtained similar EQE values of 15%, 9%, and 2% to those presented here. As such, Mes$_3$DiKTa demonstrated improved device performance in comparison to previously reported R-TADF materials, showing the highest EQE value at the relevant luminance of 100 cd m$^{-2}$ among the keto R-TADF emitters reported to date (Table 3).

3. Conclusions

Based on a new molecular engineering approach to improve the efficiency of R-TADF emitters in OLEDs, we have designed the molecule Mes$_3$DiKTa. The OLED reached an EQEmax of up to 21%. When comparing Mes$_3$DiKTa to the parent DiKTa a ~50% improvement in EQEmax is observed due to a significant reduction of aggregation-caused quenching by addition of mesityl groups to the resonant DiKTa core. By means of spin-component scaling second-order approximate coupled-cluster quantum-chemical calculations, we accurately predict $\Delta E_{ST}$ with calculated values for Mes$_3$DiKTa being 0.26 eV compared to 0.21 eV determined experimentally in 3.5 wt% mCP. The modest $\Delta E_{ST}$ value originates from the nature of the involved electronic excitations that involve short-range reorganization in the electronic density offering simultaneously large singlet radiative decay rates and small singlet-triplet exchange interactions. Remarkably, despite a very slow reverse intersystem crossing process, all triplets upconvert into singlets in electroluminescence, a result that we ascribe to the rigid nature of the emitters. This leads to improved OLED device efficiency with reduced roll-off at luminance up to 100 cd m$^{-2}$ without adversely affecting the R-TADF nature of the emitter. We further note that the improvement in device performance brought about by the use of peripheral side groups in Mes$_3$DiKTa has only a modest impact on the emission color, with CIE coordinates for blue emission similar to those measured for the DiKTa core. Finally, there is room for improvement at high luminance where efficiency roll-off remains large and we hope the strategy applied here can be further fine-tuned in the future to reduce bimolecular recombination, i.e., through the design of molecules with limited spectral overlap between singlet emission and charge and triplet absorption. Such work is currently in progress.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. The research data supporting this publication can be accessed at https://doi.org/10.17630/e717a3b6-25b6-4bd8-b1aa-9459da244707.

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 2020 research and innovation programme under the Marie Skłodowska Curie grant agreement No. 838885 (NarrowbandSSL). S.S. acknowledges support from the Marie Skłodowska-Curie Individual Fellowship. This work was funded by the EC through the Horizon 2020 Marie Skłodowska-Curie ITN project TADFlife (grant #: 812872). The St Andrews team would also like to thank the Leverhulme Trust (RPC-2016-047) and EPSRC (EP/P010482/1) for financial support. Computational resources were provided by the Consortium des Equipements de Calcul Intensif (CECI), 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 No. 1117545. A.P. acknowledges the financial support from the Marie Curie Fellowship (MIORD project, No. 748042). D.B. is a FNSR Research Director. The authors thank Franck-Julian Kahle for support with data analysis. Y.O. acknowledges fruitful discussions with Prof. Juan-Carlos Sancho-Garcia from the University of Alicante and Prof. Luca Muccioli from the University of Bologna.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

blue emission, multiresonance thermally activated delayed fluorescence, organic light emitting diodes, SCS-CC2 approach

Received: September 27, 2019
Published online: December 3, 2019
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