The design of an extended multiple resonance TADF emitter based on a polycyclic amine/carbonyl system†‡

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The development of multiple resonance thermally activated delayed fluorescence (MR-TADF) materials possessing narrow emission spectra has attracted significant attention as emitters for high colour purity organic light emitting diodes (OLEDs). In this work, a simple design strategy is introduced to construct an MR-TADF emitter, DDikTa, through dimerization of the known MR-TADF emitter DikTa. This design permits concentration quenching to be largely suppressed, which is a known weakness of previously reported MR-TADF emitters. OLEDs based on DDikTa show an EQEmax of 19% at a doping concentration of 9 wt%. The electroluminescence spectrum is red-shifted into the green, producing a rare example of a green-emitting MR-TADF OLED.

1. Introduction

Thermally activated delayed fluorescence (TADF) emitters have attracted significant attention4–5 as replacement candidates for phosphorescent organometallic complexes in organic light emitting diodes (OLEDs). Such materials are capable of recruiting 100% of the generated excitons for light production without the requirement of the heavy metal center to mediate intersystem crossing events between the excited singlet and triplet states. The most common strategy to achieve efficient TADF emitters is based on a twisted donor–acceptor molecular design6 that promotes a reduction in the exchange integral and singlet excited states (ΔEST) is achieved that then permits the thermal up-conversion of triplet excitons to singlet excitons through reverse intersystem crossing (RISC).

However, with few exceptions,7–11 the emission from TADF compounds is broad (typically, 0.45–0.55 eV; 80–110 nm), due to the charge-transfer (CT) character of the emission singlet state.12 This leads to poor colour purity in the OLED. With the increasing commercial requirements for high-resolution OLED displays, new red, green and blue emitters need to be developed that show both potential for 100% internal quantum efficiency and narrow emission spectra, obviating the use of color filters and their associated energy loss.13

Recently, a new approach to TADF emitter design was reported by Hatakeyama et al. based on p- and n-doped nanographene compounds. The first example was the rigid boron–oxygen polycyclic aromatic framework, DOBNA (see Fig. S1 for structures of literature emitters, ESI†).14 The presence of para-disposed boron and oxygen atoms in the compound possessing complementary resonance effects led to significantly separated electron densities between the HOMO and LUMO and a correspondingly small ΔEST of 0.15 eV. The emission of DOBNA unfortunately, is in the UV region, which was deemed too high in energy for this compound to be used as an emitter for OLEDs. The same group then reported the nitrogen-containing blue-emitting DABNA-1, which served as the first multiple resonance TADF (MR-TADF) emitter used in an OLED.15 OLEDs employing DABNA-1 exhibited an emission at λNL of 459 nm with an FWHM of 28 nm and the corresponding CIE coordinates of (0.13, 0.09), and with a maximum external quantum efficiency, EQEmax, of 13.5%. Further improvement in the
design was evidenced in DABNA-2, a suitably substituted analogue of DABNA-1, which produced a blue OLED with $\lambda_{\text{EL}}$ of 467 nm, an FWHM of 28 nm and CIE coordinates of (0.12, 0.13), but with a much-improved EQE$_{\text{max}}$ of 20.2%. Inspired by these early achievements, several derivatives have been reported. With the addition of $t$-butyl groups on the DABNA-1 core, $t$-DABNA shows a shorter roll-off.16 By introducing carbazole, TBN-TPA exhibited a significantly improved performance with an EQE$_{\text{max}}$ of 32.1% for a blue OLED.17 The extended polycyclic framework of $t$-DABNA results in a state-of-the-art deep blue OLED exhibiting an EQE$_{\text{max}}$ of 34.4%.18 Boranes are not the only acceptor motif used in MR-TADF emitters. Recently, ketone-containing MR-TADF emitters have been shown to produce blue to sky-blue OLEDs.19,20 We showed that by decorating a MR-TADF emitter, DiKTa, with mesityl groups, MesDiKTa, undesired aggregation caused quenching and excimer emission can be largely mitigated.21

Herein, we report the emitter DDiKTa, which is a dimeric compound consisting of two MR-TADF DiKTa units (Scheme 1). The slightly increased conjugation present in DDiKTa compared to DiKTa contributes to a modest red-shifting of the emission; however, the new compound conserves its MR-TADF status. OLEDs employing DDiKTa showed blue-green emission with $\lambda_{\text{EL}}$ of 500 nm and CIE coordinates of (0.18, 0.53) and a high EQE$_{\text{max}}$ of 19% at a doping concentration of 9 wt% in DPEPO; at a doping concentration of 12 wt%, the EQE$_{\text{max}}$ was 18.5%. To the best of our knowledge, there exists only a single report of green MR-TADF OLEDs with $\lambda_{\text{EL}}$ ranging from 493–501 nm and EQE$_{\text{max}}$ ranging from 21–22%.22 The results demonstrate how to design MR-TADF emitters exhibiting both a red-shifting of the emission and a suppression of concentration quenching in the solid state.

2. Results and discussion

2.1 Synthesis

DDiKTa was synthesized in five steps from dimethyl 2,2'- (phenylazanediyl)dibenoate (Scheme 1). Iodination with N-iodosuccinimide (NIS) gave compound 1 in high yield (83%). Saponification followed by acyl chloride formation with SOCl$_2$, and Lewis-acid catalysed Friedel–Crafts acylation afforded key intermediate 2 in 42% yield, the structure of which was confirmed by single crystal X-ray diffraction (Fig. S16, ESI†). Compound 2 was converted to the boronate ester 3 via palladium-catalyzed borylation, which was then coupled with a second equivalent of 2 under Suzuki–Miyaura cross-coupling conditions to afford DDiKTa in a moderate yield (63%).

2.2 Computational studies

The frontier molecular orbitals (the HOMO, HOMO−1, LUMO and LUMO+1, see Fig. 1) isocontour plots of DDiKTa were obtained based on the optimized ground state gas-phase geometry using Density Functional Theory (DFT) with the PBE0 functional and the 6-31G(d,p) basis set. The calculated dihedral angle between the two DiKTa moieties in DDiKTa in the ground state is around 37°. The calculated HOMO and LUMO levels of DDiKTa are −6.04 and −2.34 eV, respectively. Compared with the reference compound DiKTa, the HOMO level of DDiKTa is destabilized by 0.16 eV while the LUMO is likewise stabilized by 0.11 eV, both a result of the increased conjugation in DDiKTa. The result is a smaller ΔE$_{\text{HOMO-LUMO}}$ and an expected red-shift CT absorption compared to DiKTa as shown in Fig. S2 (ESI†) according to simulated virtual excitation.

We recently showed the importance of using a suitably high level of theory in order to accurately predict the excited state energies of MR-TADF compounds.12 Calculations using the Spin-Component Scaling Coupled-Cluster second-order approximate Coupled-Cluster (SCS-CC2) method and the cc-pVDZ level reveal that the short-range charge-transfer character of DiKTa (Fig. S2, ESI†) is inherited in DDiKTa. The calculated lowest singlet and triplet energy levels of DDiKTa are 3.39 and 3.12 eV, respectively, which are slightly lower than those of DiKTa (S$_1$ = 3.45 eV, T$_1$ = 3.18 eV) and so DDiKTa is expected to show a red-shifted emission. As a result, the same ΔE$_{\text{S}}$ of 0.27 eV indicates similar triplet harvesting ability through RISC (see Tables S1 and S2 for a summary of the excited states calculations, ESI†).

2.3 Photophysical properties

The electrochemical behavior of DDiKTa was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in degassed dichloromethane (DCM) with [nBu$_4$N]PF$_6$ as the supporting electrolyte, and the values reported versus SCE. The CV and DPV are shown in Fig. 2a and the data for oxidation/reduction potentials ($E_{\text{ox}}$/$E_{\text{red}}$) are summarized in Table S3 (ESI†). DDiKTa shows irreversible anodic and reversible cathodic waves. The $E_{\text{ox}}$ and $E_{\text{red}}$ determined from the DPV peak

![Scheme 1 Synthetic route for DDiKTa.](image-url)

Fig. 1 (a) Isocontour plots (cutoff = 0.02 a.u.) of the HOMO/HOMO−1 and LUMO/LUMO+1 orbitals calculated in the gas phase at the PBE0/6-31G(d,p) level; (b) difference density plots of S$_1$, T$_1$, and T$_2$ excited states calculated in the gas phase at the SCS-CC2/cc-pVDZ level. f indicates the oscillator strength.
phosphorescence spectra, of 0.21 eV is sufficiently small to enable a RISC process at room temperature. Fig. 2c shows the oxygen dependency on the intensity of the steady-state PL spectra. The significant drop off in intensity in the emission measured in aerated toluene compared to that after degassing with N₂ clearly demonstrates the contribution from triplet excitons. Similar to DiK-Ta and Mes3DiK-Ta, a modest positive solvatochromism was observed in Fig. 2d in the steady state PL spectra, reflective of the short-range CT state present in MR-TADF emitters.

DPEPO was identified as a suitable host matrix for OLEDs due to its high triplet energy and appropriate HOMO/LUMO levels. The steady-state and transient PL spectra were therefore investigated in 9 wt% doped films of DiK-Ta in a DPEPO matrix. This concentration was chosen as it corresponds to the doping concentration used in the optimized OLED. As shown in Fig. S5 (ESI†), a similar oxygen dependence on the intensity is also observed, analogous to that seen in toluene. The temperature-dependent steady-state emission of DiK-Ta in DPEPO is shown in Fig. 3a. The similar intensity of the PL indicates an unexpected temperature independence within the temperature range of 300–150 K, while at 77 K there is a red-shifted and structured emission that is reminiscent of the steady-state emission obtained in toluene glass at 77 K.

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 ΔE_ST, determined from the peak maxima of the fluorescence and phosphorescence spectra, of 0.21 eV is sufficiently small to enable a RISC process at room temperature. Fig. 2c shows the oxygen dependency on the intensity of the steady-state PL spectra. The significant drop off in intensity in the emission measured in aerated toluene compared to that after degassing with N₂ clearly demonstrates the contribution from triplet excitons. Similar to DiK-Ta and Mes3DiK-Ta, a modest positive solvatochromism was observed in Fig. 2d in the steady state PL spectra, reflective of the short-range CT state present in MR-TADF emitters.

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Device 1  3  492  55  5.7  23.3  13.5  9.5  0.16, 0.47  
Device 2  7  496  58  4.0  44.1  34.6  16.3  0.18, 0.52  
Device 3  9  500  59  3.7  52.4  44.4  19.0  0.18, 0.53  
Device 4  12  500  59  3.3  52.0  45.4  18.5  0.19, 0.54

* The device structure is: ITO/TAPC (35 nm)/TCTA(10 nm)/CzSi(10 nm)/DPEPO: x wt% DDiKTa(20 nm)/TmPyPB(40 nm)/LiF(1 nm)/Al. At a luminance of 1 cd m⁻².

(3.3 V), which reveals poor charge injection and mobility in the emitting layer. However, with increasing doping concentration, the turn-on voltage gradually drops to 3.3 V, which can be attributed to the better charge transporting ability of DDiKTa than that of DPEPO. Because of the imbalanced charge injection in Device 1, only an EQE max of 9.5% is obtained. Efficiencies can be optimized by increasing the doping concentration over 7 wt%.

The best performance obtained at 9 wt%, Device 3, indicates a significant suppression of concentration quenching not normally observed in MR-TADF OLEDs. The EQE max for Devices 3 is 19% with CIE coordinates of (0.18, 0.53), Table 1. Increasing the doping concentration to 12 wt% does not lead to further improvement in performance where the EQE max of Device 4 is 18.5%.

The electroluminescence (EL) spectra for these devices exhibit modest FWHM from 55 to 59 nm that increase with increasing doping concentration. The CIE chromaticity coordinates shift from (0.16, 0.47) for Device 1 to (0.19, 0.54) for Device 4; all OLEDs show green emission (Fig. 4d). In comparison with the EL of DDiKTa, the red-shifted EL of DDiKTa provides a simple design for accessing narrow green MR-TADF OLEDs.

3. Conclusions

In summary, an MR-TADF emitter DDiKTa has been developed through a simple dimerization of the previously reported emitter DDiKTa. This design maintained the multi-resonance TADF photophysical features of its corresponding monomer DiKTa. Importantly, the weakly electronically coupled DiKTa fragments that result from the twisted confirmation in DDiKTa lead to both a red-shifting of the emission and a suppression of concentration quenching, a commonly encountered problem in rigid flat molecules that are emblematic of MR-TADF emitters. The best performing OLED exhibited an EQE max of 19% with an EL maximum of 500 nm. This emitter design indicates the potential to maintain the desirable MR-TADF character of the emitter while extending the conjugation, providing an avenue to MR-TADF emitters in the green and beyond.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


