Diindolocarbazole – Achieving Multiresonant Thermally Activated Delayed Fluorescence Without The Need for Acceptor Units

David Hall, a, b* Kleitos Stavrou, c Eimantas Duda, d Andrew Danos, e Sergey Bagnich, d Stuart Warriner, e Alexandra M. Z. Slawin, a David Beljonne, b Anna Köhler, d* Andrew Monkman, c*

Yoann Olivier, f* and Eli Zysman-Colman a*

a Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, UK, KY16 9ST. E-mail: eli.zysman-colman@st-andrews.ac.uk;

http://www.zysman-colman.com

b Laboratory for Chemistry of Novel Materials, University of Mons, 7000, Mons, Belgium.

c Department of Physics, Durham University, Durham, UK, DH1 3LE. Email:

a.p.monkman@durham.ac.uk

d Soft Matter Optoelectronics, BIMF & BPI, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany. E-mail: anna.koehler@uni-bayreuth.de

e School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK

f Laboratory for Computational Modeling of Functional Materials & Solid State Physics Laboratory, Namur Institute of Structured Matter, University of Namur, Rue de Bruxelles, 61, 5000 Namur, Belgium. E-mail: yoann.olivier@unamur.be
Abstract

In this work we present a new multi-resonance thermally activated delayed fluorescence (MR-TADF) emitter paradigm, demonstrating that the structure need not require the presence of acceptor atoms. Based on an in-silico design, the compound DiICzMes₄ possesses a red-shifted emission, enhanced photoluminescence quantum yield, and smaller ΔE_ST than the parent indolocarbazole that induces MR-TADF properties. Coupled cluster calculations accurately predict the magnitude of the singlet-triplet energy gap, ΔE_ST, when the optimized singlet and triplet geometries are used. Slow yet optically detectable reverse intersystem crossing contributes to low efficiency in organic light-emitting diodes using DiICzMes₄ as then emitter. However, when used as a terminal emitter in combination with a TADF assistant dopant within a hyperfluorescence device architecture, maximum external quantum efficiencies of up to 16.9% were achieved at CIE (0.15,0.11). This represents one of the bluest hyperfluorescent devices reported to date. Simultaneously, recognising that MR-TADF emitters do not require acceptor atoms reveals an unexplored frontier in materials design, where yet greater performance may yet be discovered.

Introduction

The organic light emitting diode (OLED) field has taken another step forward with the introduction of multiresonant thermally activated delayed fluorescent (MR-TADF) materials.¹ As with conventional donor-acceptor (D-A) TADF emitters, MR-TADF compounds possess suitably small singlet-triplet energy gaps (ΔE_ST) to permit triplet excitons to be up-converted to singlets by reverse intersystem crossing (RISC), unlocking considerably improved device efficiency in OLEDs²-⁴ alongside applications in several other optoelectronic contexts.⁵-⁸ RISC is achieved in D-A TADF materials through reducing the exchange integral by electronically decoupling the donor and acceptor moieties as a result of a highly twisted conformation,²,⁴ with the HOMO situated on the donor and LUMO on the acceptor, combined with vibronic coupling between local and charge transfer triplet states to facilitate spin orbit coupling.⁹ Due to conformational flexibility inherent in these classes of emitter, the charge-transfer emission bands are particularly broad, resulting in poor colour purity of resulting OLEDs and extreme challenges in achieving deep-blue colour coordinates.¹⁰
For MR-TADF emitters the HOMO-LUMO separation and thus small $\Delta E_{ST}$ are achieved via a complementary pattern of the electron density distribution on adjacent atoms within the molecule between HOMO and LUMO states, made possible by the incorporation of suitably positioned electron-donating and electron-withdrawing atoms (or functional groups). The reorganization of the electron density upon excitation is relatively localized, so that the lowest singlet and triplet excited states possess short-range charge transfer (SRCT) character. The small exchange integral in MR-TADF compounds is best illustrated with difference density plots (Figure 1). Seemingly paradoxically for charge-transfer states, there is also a suitably large overlap in the excited and ground state wavefunctions, leading to larger oscillator strengths for the $S_1$-$S_0$ transition and thus fast radiative decay rates, $k_r$. We note that the wavefunction will be of mixed locally excited (LE) and CT character, and in this case the LE contribution appears to dominate, thus coupling to the ground state is high but electron exchange energy remains sizeable. Combined with conformationally rigid structures these SRCT states confer a very narrow emission spectrum with full width at half maxima (FWHM) below 30 nm, leading to much greater colour purity, which is required for high-definition displays and advantageous for achieving deep-blue emission.

MR-TADF materials DABNA-1 and DABNA-2 were first reported in 2016 by Hatakeyama and co-workers. These compounds contain a central accepting boron atom and para-disposed donating nitrogen atoms that achieve the desired alternating pattern of the electron density distribution. OLEDs employing DABNA-1 and DABNA-2 showed maximum external quantum efficiencies, EQE$_{\text{max}}$, of 13.5% and 20.2% with Commission Internationale de l’Éclairage, CIE, coordinates of (0.13, 0.09) and (0.12, 0.13), respectively. Low RISC rates (compared to contemporaneous D-A-D emitters) in this early work resulted in severe efficiency roll-off though, with efficiencies at 1,000 cd m$^{-2}$ not reported. A large number of other MR-TADF materials use this same design template have since been reported.
Dramatic improvements in both EQE$_{\text{max}}$ and efficiency roll-off were recently reported for the extended system ν-DABNA (Figure S1).$^{21}$ This compound contains two DABNA-1 units that are fused together, extending the π conjugation (Figure 1), which results in a smaller ΔE$_{\text{ST}}$ from 0.18 eV in DABNA-1 (in 1 wt% mCBP)$^{13}$ to 0.02 eV (in 1 wt% DOBNA-OAr).$^{21}$ OLEDs made with this emitter show an outstanding EQE$_{\text{max}}$ of 34.4% at CIE (0.12, 0.11), assisted in part by spontaneous emitter alignment improving device optical outcoupling, as confirmed by angularly-resolved emission measurements in a later work.$^{22}$ Further, due in part to its small ΔE$_{\text{ST}}$ and class-leading RISC rates, the device shows superior efficiency roll-off, with an EQE at 1,000 cd m$^{-2}$ of 26.1% (Table S1).

Another family of MR-TADF compounds, introduced by Zhang et al. in 2019,$^{23}$ relies on boron and nitrogen atoms to direct the electron density pattern, but these compounds incorporate fused donor units, such as in CzBN. The fused system results in increased electronic delocalisation, thus stabilizing S$_1$, which produces a red-shift in the emission (Figure 1). The first series of emitters incorporated peripheral electron-withdrawing groups onto the CzBN core, which led to a further red-shift of the emission. OLEDs with 2F-BN, 3F-BN and 4F-BN showed EQE$_{\text{max}}$ of 22.0%, 22.7% and 20.9%, respectively, at CIE of (0.16, 0.60), (0.20, 0.58) and (0.12, 0.48), representing the first examples of green-emitting MR-TADF OLEDs. Following this early work a range of materials based on this molecular design have been reported;$^{23-28}$ the OLED with BBCz-G showing the highest efficiencies, with an EQE$_{\text{max}}$ of 31.8% at CIE of (0.26, 0.68).$^{29}$ This design was also used to produce the first examples of red-emitting MR-TADF compounds, BBCz-R$^{29}$ and R-(T)BN$^{30}$ (Figure S1). The red-shifted emission in both examples results from the positioning of the donating nitrogen atoms, and thus the withdrawing boron atoms, para to each other, thereby inducing partial bonding and antibonding character and resulting in a smaller HOMO-LUMO gap, ΔE, and a much lower energy emissive S$_1$ state$^{30}$. Devices with these three emitters showed EQE$_{\text{max}}$ surpassing 20% at CIE coordinates of (0.67, 0.33)$^{29}$ and (0.72, 0.18)$^{30}$. Another route to colour tuning has been the addition of electron donating and withdrawing substituents on the CzBN core, with blue- or red-shifts of the emission possible depending on the position and number of additional donors and acceptors.$^{27,29,31,32}$
An alternative core unit based on DABNA-1 was presented firstly by Oda et al., where the positions of boron and nitrogen atoms are switched (ADBNA-Me-Mes and ADBNA-Me-Tip, Figures 1 and S1). Having two boron and one nitrogen atom results in a smaller $\Delta E$ compared to that of DABNA-1; however, there was minimal impact on $\Delta E_{ST}$ (Table S1). The resulting OLEDs showed CIE of (0.10, 0.27) and (0.11, 0.29) for ADBNA-Me-Mes and ADBNA-Me-Tip, respectively. The EQE$_{\text{max}}$ for these devices are 16.2% and 21.4%, respectively, while efficiency roll-off was modest, with EQE$_{100}$ of 11.2% and 15.4%.

Another family of MR-TADF compounds contains carbonyl groups in lieu of boron atoms as the electron acceptor. The first example, QAO, reported in 2019, translated into devices with an EQE$_{\text{max}}$ 19.4% at CIE (0.13,0.18). We showed that decoration of this core with mesityl groups, MesDiKTa, can mitigate aggregation induced quenching (AIQ), which is a common problem with these planar molecules. With this emitter, the OLED showed the highest EQE$_{\text{max}}$ for this family of compounds of 21.1% at CIE of (0.12, 0.32). A dimeric structure, 3MTPTOAT, based on a related core, TOAT, which itself has previously been reported as a room temperature phosphorescent emitter, was used as the emitter in an OLED that showed a very high EQE$_{\text{max}}$ of 31.2%. A range of emitters has now been reported incorporating carbonyl groups within the molecular design; however, most of these emitters show relatively large $\Delta E_{ST}$ and the devices often show EQE$_{\text{max}}$ values inferior to 20%. A full summary of the discussed literature emitters including structures, photophysical data and OLED device performances can be found in Figure S1 and Table S1.

Despite the excellent characteristics of MR-TADF emitters, the majority of MR-TADF emitters have a low $k_{\text{RISC}}$, with most around $10^4$ s$^{-1}$ (Table S2). The slow $k_{\text{RISC}}$ has proved detrimental to device performance with most OLEDs using the MR-TADF compound as an emitter suffering from large efficiency roll-off$^{13}$ In the literature only two examples exist where $k_{\text{RISC}}$ surpasses $10^6$ s$^{-1}$ (Figure S2),
$m$-CzBNCz$^{27}$ and BSBS-N1$^{38}$, where $k_{\text{RISC}}$ reaches 1.08 and $1.90 \times 10^6$ s$^{-1}$ respectively. Even direct comparison between reported RISC rates from different research teams is challenging though, due to the plurality of reported methods for determining its value$^{39}$ and subtle yet important practical concerns.$^{40}$ The MR-TADF emitters with the fastest $k_{\text{RISC}}$ are nevertheless two orders of magnitude slower than the best performing D-A TADF emitter (Figure S2). This was predicted by Northey and Penfold$^{41}$ and experimentally shown by Stavrou et al.,$^{42}$ that the RISC mechanism in MR-TADF systems occurs through crossing between $T_1$ and an upper triplet state via reverse internal conversion. This involves closely-lying triplet states and requires new design rules for new chemical structures with optimal efficiency. A large factor in this apparent gap in RISC rates is that the chemical space explored for MR-TADF emitters remains small compared to the thousands of donor-acceptor TADF compounds reported. Furthermore, we recently demonstrated$^{11}$ that time-dependent DFT calculations, which are commonly used to predict the nature and the energies of the excited singlet and triplet states of D-A TADF compounds,$^{43}$ do not accurately predict these parameters for MR-TADF compounds, thus hindering computationally guided molecular design. We have shown repeatedly that coupled cluster calculations,$^{36, 44-46}$ which include double excitation contributions, perform significantly more accurately, albeit at a higher computational cost.

Here, we apply the same coupled cluster methodology to guide the design of a new class of MR-TADF materials, which surprisingly do not require an electron-accepting functionality within the compound. Despite the lack of acceptor atom, a complimentary pattern of increasing and decreasing electron density is achieved for $S_1$ (but not necessarily for $T_1$) compared to $S_0$ in this class of emitters. DiICzMes$_4$ was also compared to two smaller reference emitters, ICz and ICzMes$_3$, with mesityl groups in DiICzMes$_4$ intended to suppress AIQ.$^{36}$ Compared to ICz and ICzMes$_3$, the expansion of the $\pi$-system in DiICzMes$_4$ ensures a further decrease of HOMO-LUMO overlap and results in a much smaller $\Delta E_{\text{ST}}$, reduced from 0.47 eV in ICz to 0.26 eV in DiICzMes$_4$ (in toluene). Further, there is a desirable increase in $\Phi_{\text{PL}}$ across the series from 37%, 56% and 67%, accompanied with a red-shift in the emission maximum, $\lambda_{\text{PL}}$, from 374 nm, 387 nm and 441 nm in 3 wt% PMMA films, for ICz, ICzMes$_3$ and
DiICzMes$_4$, respectively, all in agreement with recent SCS-CC2 calculations for B/N-doped nanographenes.$^{11}$

Crucially, although the core DiICz structure decorated with 'Bu groups has recently been reported,$^{47,48}$ its identity as a TADF emitter – confirmed here by time-resolved photophysical measurements – was overlooked until recently.$^{49}$ An analogous non-fused tricarbazole-amine system (TCA_C4) had previously been shown to have a small singlet triplet gap, 0.21 eV, and gives moderate thermally activated DF via a reverse internal conversion, upper triplet state crossing mechanism.$^{50}$ It is only recently that the MR-TADF mechanism has been elucidated to take place through a similar rIC mechanism in ν-DABNA,$^{42}$ and presumably also other MR-TADF emitters. Nonetheless, in both previous reports of the DiICz structure the compound was presented as a purely fluorescent system (named pICz$^{47}$ and 5$^{48}$), with relatively large $\Delta E_{ST}$ of 0.29 eV. Recently, a similar derivative, tPBisICz, was introduced as a MR-TADF emitter, and the authors contended that RISC proceed between T$_2$ and S$_1$.$^{49}$ The device showed an EQE$_{\text{max}}$ of 23.1% at CIE (0.15, 0.05); however, efficiency roll-off was severe and this is likely due to the inefficient $k_{\text{RISC}}$ of $1.4 \times 10^3$ s$^{-1}$. Although the RISC rate for DiICzMes$_4$ is slow (similar to that of TCA_C4$^{50}$), this work supports the existence of an entirely new subcategory of ‘acceptor-free’ MR-TADFs, which may yield improved performance in device applications in future.
Figure 1. Evolution of MR-TADF emitters including simplified difference density plots for each core.

Results and Discussion

Modelling

Initial ground state optimisation followed by vertical excitation were performed at the SCS-CC2/cc-pVDZ level of theory. Indolocarbazole (ICz) has been frequently used by the TADF community, able to act as both a donor or acceptor depending on the nature of the substituents. $\Delta E_{ST}$ was predicted to be 0.33 eV, which is high for TADF materials but rationalized by the different nature of $S_1$ and $T_1$ excited states. Indeed, $S_1$ displays a typical difference density pattern characteristic of a SRCT excited state while $T_1$ exhibits a locally excited (LE)-like pattern, with the latter more stabilized, hence the large $\Delta E_{ST}$ (Figure 2). It has been inferred previously that extending the MR-TADF electronic delocalisation...
could be a viable strategy to decrease $\Delta E_{ST}$ at the same time as increasing the oscillator strength. Based on this hypothesis, four derivatives of ICz were modelled, with differing patterns of the relative position of the nitrogen atoms: DiICz-m-1, DiICz-m-2, DiICz-p-1 and DiICz-p-2. Compared to the parent ICz, each of these four emitters had a stabilized $S_1$ state, decreasing from 3.78 eV for ICz to 3.58 eV, 3.57 eV, 3.36 eV and 3.32 eV for DiICz-m-1, DiICz-m-2, DiICz-p-1 and DiICz-p-2, respectively, the result of delocalization of the $S_1$ wavefunction (see Figure 2). As previously reported for other MR-TADF emitters, when the donating nitrogen atoms are located para to each other the red-shift is the largest. The para-derivatives here also had the smallest predicted $\Delta E_{ST}$ of 0.17 eV and 0.15 eV for DiICz-p-1 and DiICz-p-2, respectively, while $\Delta E_{ST}$ is 0.30 eV and 0.32 eV for DiICz-m-1 and DiICz-m-2.

Of DiICz-p-1 and DiICz-p-2, DiICz-p-2 has a considerably larger oscillator strength of 0.15 compared to 0.01 in DiICz-p-1 and thus this motif was assessed as the most promising. Furthermore, we have previously demonstrated that addition of mesityl groups can mitigate AIQ, which plagues MR-TADF
materials\textsuperscript{42} (and many other similar systems\textsuperscript{52, 53}) owing to their planar and electron-rich geometries. With this in mind, we designed the mesityl derivative of ICz, ICzMes\textsubscript{3}. In this compound the mesityl groups have the added benefit of reducing $\Delta E_{ST}$ (calculated for vertical transitions from the ground state geometry) from 0.33 eV to 0.21 eV. The decrease in $\Delta E_{ST}$ is essentially the result of preferential stabilization of $S_1$ while the energy of $T_1$ energy is only minimally affected (Figure S29). The small stabilization of $T_1$ in ICzMes\textsubscript{3} can be explained by the absence of significant orbital contributions from the carbon atoms connecting the mesityl groups in the $T_1$ difference density pattern (Figure S29). We also investigated the role that decoration with mesityl groups would play on the core structure of DiICz-p-2, which together form the target material DiICzMes\textsubscript{4}. In DiICzMes\textsubscript{4} (Figure S29), the mesityl substitution helps to reduce the predicted $\Delta E_{ST}$ from 0.15 eV to 0.13 eV for similar reasons as described for ICzMes\textsubscript{3}. Due to the close energy of LE $T_1$ and the SCRT $T_2$ states of the DiICz-p-2, substitution by the four mesityl groups allows inversion between the two. $T_1$ becomes SCRT in DiICzMes\textsubscript{4} possessing similar, yet slightly different character than $S_1$.

In contrast to previously investigated MR-TADF emitters, we see large changes when comparing $\Delta E_{ST}$ computed from vertical excitation from the ground state geometry and experiments due to the different nature of $T_1$ and $S_1$ states (see difference density plots in Figure S27). In such a case, relaxation of the excited states could be key to reach quantitative agreement with the experiments. We thus optimized both the $S_1$ and $T_1$ states within the TDA using PBE0 functional and 6-31G(d,p) basis set, and compute the $T_1$ and $S_1$ excited state energies at the SCS-CC2/cc-PVDZ level of theory for ICz, ICzMes\textsubscript{3} and DiICzMes\textsubscript{4} as well as for three literature MR-TADF compounds, DABNA-1, BCzBN and DiKTa. Quantitative agreement with the experiments is reached with $\Delta E_{ST}$ increasing for ICz, ICzMes\textsubscript{3} and DiICzMes\textsubscript{4}, to 0.59 eV, 0.45 eV and 0.29 eV (Figure 3), respectively caused by a larger relaxation energy of the $T_1$ state in line with a greater LE character for this state (Tables S6 – S10). Interestingly, such an increase in $\Delta E_{ST}$ does not manifest for DABNA-1, BCzBN and DiKTa, wherein $\Delta E_{ST}$ is only shifted by a maximum of 0.04 eV, owing to the similar SRCT nature of $T_1$ and $S_1$ (see Tables S6 – S10 and Figure S30). The similar orbital character of $S_1$ and $T_1$ in many previous emitters, and the ones
presented here, implies that RISC between these two states is not symmetry allowed according to El Sayed’s rules. Thus, RISC must occur via a spin-vibronic mechanism involving intermediate triplet states lying between S₁ and T₁. Irrespective of the starting geometry, a close lying triplet state of different orbital type is present, whose involvement has been shown to contribute to the MR-TADF RISC mechanism. Both smaller ΔE_ST and ΔE_T2T1 were observed, decreasing across the series from ICz, ICzMes₃ and DiICzMes₄. We observed again a decreased ΔE_ST upon incorporation of mesityl groups from 0.59 eV for ICz to 0.45 eV ICzMes₃. Unlike previously reported MR-TADF emitters that contain acceptor atoms/groups, for this class it is essential to optimise the excited states in order to achieve quantitative agreement with experimental ΔE_ST.
Figure 3. Structures, excited state energies and difference density plots of each $S_1$ and $T_1$ for ICz (left panel), ICzMes$_3$ (central panel) and DiICzMes$_4$ (right panel) from excited state optimized geometry.

Synthesis

The materials were synthesised through a multistep reaction sequence outlined in Figure 4. Carbazole was coupled to 2-bromofluorobenzene under $S_{NAr}$ conditions at elevated temperatures in an excellent
yield of 96%. Intramolecular oxidative ring closing using Pd(OAc)$_2$ afforded ICz in a good yield of 85%. Subsequent electrophilic bromination using NBS afforded intermediate ICzBr$_3$ in 79% yield, which was then decorated with mesityl groups using a Suzuki-Miyaura coupling reaction, producing ICzMes$_3$ in a good yield of 69%. A similar Suzuki-Miyaura coupling was employed to obtain CzMes$_2$ from dibromocarbazole in 62% following a literature procedure. Intermediate 2 was obtained in 75% via an SN$_{Ar}$ reaction that proceeded at lower temperature (50 °C). Double oxidative cyclization using Pd(OAc)$_2$ generated DilCzMes$_4$ in 59% yields. Crystals of ICzMes$_3$ and DilCzMes$_4$ were grown from slow evaporation of methanol into a saturated solution of toluene over several days. Packing in ICzMes$_3$ is primarily governed by π–π stacking interactions between mesityl groups on adjacent molecules (Figure S23). For DilCzMes$_4$ π–π stacking occurs between the mesityl group of one molecule and the DilCz core of an adjacent molecule. The ICz unit in both compounds was not perfectly flat (Figure 4).

Figure 4. Synthesis of (a) the emitters and crystal structures of (b) ICzMes$_3$ and (c) DilCzMes$_4$. 
Optoelectronic characterization

The electrochemical properties were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in DCM for oxidation and DMF for reduction (Figure 5a), with the electrochemical potentials reported versus SCE (}
Table 1). ICz showed irreversible oxidation and reduction waves with the former appearing to undergo polymerisation, which has been previously reported for ICz\textsuperscript{55} and seen in other carbazole-containing emitters.\textsuperscript{56} Addition of the mesityl groups in ICzMes\textsubscript{3} renders the oxidation pseudoreversible in a similar manner to what was previously observed for Mes\textsubscript{3}DiKTa,\textsuperscript{36} with \(E^{\text{ox}}\) at 1.45 V versus 1.43 V for ICzMes\textsubscript{3}. Indeed, McNab \textit{et al.} had demonstrated that the electrochemical instability of ICz is associated with dimer formation centred at the \textit{para} positions.\textsuperscript{55} There is likewise little change in the irreversible reduction waves with reduction potentials of these two compounds, \(E^{\text{red}}\), at -2.21 V and -2.16 V for ICz and ICzMes\textsubscript{3}, respectively. By contrast, both oxidation and reduction waves for DiICzMes\textsubscript{4} are largely reversible. The oxidation wave is cathodically shifted to 1.11 V while the reduction wave is anodically shifted to -1.92 V, both a reflection of the larger conjugation length of this molecule compared to ICz and ICzMes\textsubscript{3}. This produced a significant reduction in the redox gap, \(\Delta E_{\text{redox}}\), in agreement with calculations, where the calculated \(\Delta E\) decreases from 4.65 eV and 4.50 eV for ICz and ICzMes\textsubscript{3} to 3.86 eV in DiICzMes\textsubscript{4}. The trends in HOMO and LUMO values are corroborated at the DFT level (Table S4 and Table S11).
Table 1. Solution optoelectronic data of each emitter

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<th>$T_1$ / eV</th>
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*a* Toluene at 300 K, *b* Values in parentheses are the FWHM, *c* In degassed toluene measured an integrating sphere under N$_2$, values in parentheses are in air-saturated solution, $\lambda_{\text{exc}} = 330$ nm, *d* From the onset of the steady-state emission and phosphorescence in toluene glass at 77 K, $\lambda_{\text{exc}} = 330$ nm, *e* Energy difference between the onset of the steady-state and phosphorescence at 77 K, *f* $\lambda_{\text{exc}} = 355$ nm, *g* The HOMO and LUMO energies were determined according to $\text{E}_{\text{HOMO/LUMO}} = -(\text{E}_{\text{ox on}st} / \text{E}_{\text{red on}st} + 4.8)$ eV, *h* $\lambda_{\text{exc}} = 320$ nm, *i* $\lambda_{\text{exc}} = 380$ nm, *j* $\lambda_{\text{exc}} = 350$ nm, *k* $\lambda_{\text{exc}} = 350$ nm.

We next investigated the photophysical properties of the three emitters in solution. The UV-Vis absorption data in toluene (PhMe), 2-methyltetrahydrofuran (2-MeTHF), ethyl acetate (EtOAc), dichloromethane (DCM) and dimethylformamide (DMF) can be found in Figure S31 and Tables S12 – S14. The polarity of the solvent had minimal impact on the absorption spectra, with nearly identical
absorption maxima, $\lambda_{\text{abs}}$, and molar absorptivity values, $\epsilon$, regardless of solvent. Using the representative data in toluene (Table 1), there is a high intensity, low energy band at 364 nm, 379 nm and 431 nm for ICz, ICzMes$_3$, and DiICzMes$_4$, respectively, assigned by calculations to a SRCT band; there is a second distinguishable band at smaller $\epsilon$ at 350 nm, 363 nm and 410 nm, respectively, that is likely due to a transition to a different vibronic level of the S$_1$ state based on the ca. 0.15 eV energy gap between these two bands. Both ICz and ICzMes$_3$ possess higher energy bands at 320 nm and 330 nm of similar $\epsilon$, which we assign to transitions to the S$_2$ state. The similar $\epsilon$ values are captured at the SCS-CC2 level where both S$_1$ and S$_2$ have similar oscillator strengths, $f$, of 0.10 and 0.09 for ICz and 0.14 and 0.13 for ICzMes$_3$. A far greater oscillator strength of 0.66 is predicted for the transition to S$_2$ for DiICzMes$_4$ compared to that to S$_1$ ($f = 0.21$). Indeed, the band at 365 nm possesses a significantly larger $\epsilon$ of $39 \times 10^4$ M$^{-1}$ cm$^{-1}$ compared to that at 431 nm ($\epsilon = 11 \times 10^4$ M$^{-1}$ cm$^{-1}$), suggesting a greater degree of LE character for the transition associated with this band.

Figure 5. Solution-state optoelectronic data. a) CV (solid line) and DPV (dashed) where where the anodic scan is in DCM and the cathodic scan is in DMF, with 0.1 M $[n$Bu$_4$N]$PF_6$ as the supporting electrolyte and Fc/Fc$^+$ as the internal reference (0.46 V for DCM and 0.45 for DMF vs. SCE)$^{58}$; b) Steady-state PL in toluene, at concentrations of 0.6 – 2.0 $\times$ 10$^{-5}$ M, where $\lambda_{\text{exc}} = 320$ nm for ICz and ICzMes$_3$ and $\lambda_{\text{exc}} = 380$ nm for DiICzMes$_4$, and pictures of each in solution (ICz, ICzMes$_3$ and DiICzMes$_4$) left to right.
Minimal changes in emission energy and band shape were observed upon modulation of the solvent polarity (Figure S31 and Tables S12 – S14). Such behaviour is characteristic of MR-TADF emitters, which undergo emission from a SRCT excited state.\textsuperscript{11} Owing to their rigid nature, the emission is narrow and the Stokes shifts are small (10, 8, and 10 nm, respectively, for ICz, ICzMes\textsubscript{3} and DiICzMes\textsubscript{4}) reflecting the very small reorganisation energy between the ground and excited state. The corresponding FWHM for the PL spectra in toluene are 21 nm, 21 nm and 17 nm for ICz, ICzMes\textsubscript{3} and DiICzMes\textsubscript{4}, respectively. There are low energy shoulders apparent in the steady-state PL of all three emitters. This shoulder is assigned to a vibronic shoulder (\textit{vide infra}) (Figure S34d).

The energies of the singlet and triplet states, and hence, $\Delta E_{ST}$, were determined based on the high-energy onset of the prompt fluorescence and phosphorescence spectra obtained at 77 K in toluene glass. In all cases, the phosphorescence is very well vibrationally structured and characteristic of a carbazole moiety in strong contrast with respect to the fluorescence supporting the different nature of the S\textsubscript{1} and T\textsubscript{1} excited states. There is a progressive decrease in $\Delta E_{ST}$ of 0.47 eV, 0.39 eV and 0.26 eV for ICz, ICzMes\textsubscript{3} to DiICzMes\textsubscript{4}, respectively, a trend that is well reproduced by SCS-CC2 calculations when considering optimized excited state structures (Table S10). We simulated the vibronically resolved fluorescence and phosphorescence spectra for DiCz-p-2 (we omitted the mesityl groups from DiICzMes\textsubscript{4} to avoid spurious negative vibration modes) and obtain excellent agreement with the corresponding experimental spectra of DiICzMes\textsubscript{4} (see Figure S33). The lower energy shoulder of the fluorescence spectrum observed experimentally is attributed to a vibronic transition based on the cross-comparison with the simulated one. This shoulder disappears with increasing concentration when aggregate emission begins to contribute significantly to the emission spectrum (Figure S35d). Furthermore, the simulated vibronically-resolved phosphorescence spectrum is also in excellent agreement with the experiment. Interestingly, there is an enhanced vibronic intensity associated with high-frequency (1200-1600 cm\textsuperscript{-1}) vibrations in the phosphorescence spectrum in comparison to fluorescence spectrum. This reflects the more pronounced geometric relaxation taking place in T\textsubscript{1} compared so S\textsubscript{1}, which translates into a larger adiabatic $\Delta E_{ST}$ in comparison to the vertical $\Delta E_{ST}$ (Table
and provides a clear spectroscopic evidence for the different character of the $S_1$ and $T_1$ excited states. This behavior is again in strong contrast with most of the MR-TADF emitters previously reported in the literature.

The solution photoluminescence quantum yields increased from 58%, 66% and 70% for ICz, ICzMes$_3$ to DiICzMes$_4$, respectively, again reflecting expected trends in the calculations. Time-resolved PL decays revealed prompt CT lifetimes of 15.0 ns, 21.6 ns and 40.5 ns for ICz, ICzMes$_3$ and DiICzMes$_4$, respectively. A small contribution of delayed emission was observed for ICz, which was ascribed to originate from TTA (Figure S32b), while no delayed emission was observed for either ICzMes$_3$ or DiICzMes$_4$.

We next investigated the solid-state PL behaviour in a wide bandgap host, PMMA at 3 wt% doping of emitter. The $\lambda_{PL}$ are 377 nm, 391 nm and 442 nm for ICz, ICzMes$_3$ and DiICzMes$_4$, respectively, values that are modestly red-shifted compared to those in toluene. The $\Delta E_{ST}$ values are similar to those measured in toluene of 0.50 eV, 0.41 eV and 0.29 eV for ICz, ICzMes$_3$ and DiICzMes$_4$, respectively, and align with the calculated $\Delta E_{ST}$ using optimized excited state structures. The $\Phi_{PL}$ are similar to those in toluene at 37%, 58% and 67%, for ICz, ICzMes$_3$ and DiICzMes$_4$, respectively. Again, a red-shifted emission, a decreased $\Delta E_{ST}$ and an improved $\Phi_{PL}$ are observed across the series from ICz to ICzMes$_3$ and to DiICzMes$_4$ (Figure S34). Owing to their large $\Delta E_{ST}$ and excessive $S_1$ energies, the photophysical properties of ICz and ICzMes$_3$ were not investigated in other hosts.

We next investigated the photophysical properties of DiICzMes$_4$ in mCP as this OLED-compatible host matrix has a suitably large $T_1$ energy of 2.9 eV. The optimum doping concentration as a function of $\Phi_{PL}$ was determined (Figure 6a and Table S15). No AIQ was observed up to 3 wt%, with $\Phi_{PL}$ maintained at 82%; beyond this concentration the $\Phi_{PL}$ decreased, with neat films showing a $\Phi_{PL}$ of 30% (Figure 6a). The FWHM of a drop-cast 3 wt% doped film in mCP was larger at 40 nm; a low-energy shoulder
increased in intensity with increasing doping, which we assigned to an emission from an aggregate (Figure S35d). However, when films were spin-coated, the aggregate formation could be suppressed, with 3 wt% spin-coated films having a FWHM of 21 nm at $\lambda_{PL}$ 451 nm. At this concentration the $\Delta E_{ST}$ is 0.26 eV, leading to a long $\tau_d$ of 433 $\mu$s but with a delayed emission suppressed at low temperatures (Figure 6c). A similar behavior exists when DiICzMes$_4$ is doped in DPEPO at 5 wt% where the delayed emission is no longer observed below 80 K (Figure S36b). In the time-resolved measurements the spectra of the delayed emission match that of the prompt fluorescence, and thus can be assigned to emission from the $S_1$ state rather than any room temperature phosphorescence, which has been observed in other rigid systems$^{60}$ (Figure S35b). TTA was ruled out as the emission mechanism owing to the linear power dependence of the emission intensity (Figure 6d).$^{61}$

The contribution of the delayed emission to the overall emission is often small in MR-TADF emitters, reflecting the efficient $k_s^5$ (and small $\Phi_{ISC}$) and the slow $k_{RISC}$. For instance, for DABNA-1 and DiKTa the $\Phi_d$ is around 4% for 1 wt% DABNA-1$^{13}$ in mCBP and 1% for DiKTa in toluene.$^{56}$ For DiICzMes$_4$, the $\Phi_d$ is 1.2%, and thus $k_{RISC}$ is slow in this emitter, at $1.8 \times 10^3$ s$^{-1}$ following the methodology of Masui et al.$^{62}$ This is substantially slower than most MR-TADF emitters, but similar to tPBisICz and tBisICz, which were reported as 1.4 and $0.14 \times 10^3$ s$^{-1}$, respectively, in 1 wt% mCP:TSPO1 films.$^{49}$ In this work, neither ICz nor ICzMes$_3$ show TADF due to their too large $\Delta E_{ST}$ of 0.47 eV and 0.39 eV, respectively, measured in toluene glass; however, DiICzMes$_4$ shows weak TADF as its $\Delta E_{ST}$ of 0.26 eV is much smaller.
Figure 6. Solid-state photophysics of DilCzMes. a) $\Phi_{\text{PL}}$ as a function of doping concentration, calculated using an integrating sphere. An exponential decay has been fitted to guide the reader, $\lambda_{\text{exc}} = 350$ nm; b) Steady-state (SS) emission spectra at RT ($\lambda_{\text{exc}} = 330$ nm) and 77 K and phosphorescence spectrum at 77 K in 3 wt% mCP films, ($\lambda_{\text{exc}} = 350$ nm); c) Temperature-dependent time-resolved PL decays in 3 wt% mCP films, $\lambda_{\text{exc}} = 355$ nm; d) Intensity dependence as a function of laser power in 3 wt% mCP, $\lambda_{\text{exc}} = 355$ nm.

Table 2. Solid-state photophysical properties.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{PL}}$ (FWHM) / nm</th>
<th>$\Phi_{\text{PL}}$ / %</th>
<th>$S_1$ / eV</th>
<th>$T_1$ / eV</th>
<th>$\Delta E_{\text{ST}}$ / eV</th>
<th>$\tau_p$ / ns</th>
<th>$\tau_d$ / $\mu$s</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICz</td>
<td>377 (29)</td>
<td>37</td>
<td>3.38</td>
<td>2.88</td>
<td>0.50</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>ICzMes3</td>
<td>391 (28)</td>
<td>58</td>
<td>3.26</td>
<td>2.85</td>
<td>0.41</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
In 3 wt% doped PMMA films, \( \lambda_{\text{exc}} = 330 \text{ nm} \), where value in parentheses is FWHM. Determined using an integrating sphere, \( \lambda_{\text{exc}} = 330 \text{ nm} \), \( S_1 \) and \( T_1 \) determined from the onset of the steady-state and phosphorescence spectra, respectively, at 77 K, \( \lambda_{\text{exc}} = 330 \text{ nm} \), Calculated from the energy difference between the energies of the \( S_1 \) and \( T_1 \) states at 77 K, \( \lambda_{\text{exc}} = 355 \text{ nm} \), \( \lambda_{\text{exc}} = 350 \text{ nm} \), \( \lambda_{\text{exc}} = 350 \text{ nm} \), In 3 wt% doped mCP films.

In anticipation of OLED applications, additional time-resolved emission decays were also collected for DiICzMes\(_4\) in a wide range of high-triplet OLED hosts (Figure S36). For these experiments 10% loading in drop-cast films was used, improving the overall signal but also enhancing the emission detectable from redshifted dimer or excimer species, as evident in the individual normalised spectra (Contour plots, Figure S36c). In line with the stationary emission spectra of MR-TADF materials in varying solvent polarity (Figure S31), we observe only minor differences in the time-resolved spectra and decays regardless of host.

**Devices**

Regioisomeric derivatives of DiICz have been reported in the form of 4, 48 \( m\)-FLID\(_{63}\) and tDIDCz\(_{64}\), where each was described as a traditional fluorescent emitter. Large experimentally determined \( \Delta E_{\text{ST}} \) values of 0.36 eV and 0.44 eV were reported for \( m\)-FLID\(_{63}\) and tDIDCz\(_{64}\) respectively, in frozen THF glass. The corresponding UV-emitting OLEDs showed EQE\(_{\text{max}}\) of 5.2% and 3.3% at CIE of (0.16, 0.03) and (0.16, 0.02), respectively. Having confirmed the previously overlooked though admittedly weak TADF activity of DiICzMes\(_4\), its use as an emitter in OLEDs was assessed. Devices using a stack of ITO (HIL/anode) | NPB (HTL, 40nm) | TSBPA (EBL, 10nm) | DiICzMes\(_4\):DPEPO 10% (EML,
30nm) | DPEPO (HBL, 10 nm) | TBPi (ETL, 40nm) | LiF (EIL, 1nm) | Al (cathode, 100nm) were fabricated (Figure 7), with representative performance shown in Figure 7. These results show that the low rate of RISC in DiICzMes4 is insufficient to enable efficient triplet harvesting even at the lowest current densities (and corresponding lowest brightness, ~10 cd m⁻²) investigated here. The resulting low EQE values are consistent with the DiICzMes4 acting akin to a fluorescent dopant, only able to harvest singlet excitons for emission with an upper limit of EQE max < 5%. This result is also in-line with what was observed for previous acceptor-free rIC DF material TCA_C4.50 The OLED shows CIE coordinates of (0.15, 0.11). Despite the high EQE max observed for tPBisICz, efficiency roll-off was severe with the EQE at 100 cd m⁻² only about 5% while the EQE at 1,000 cd m⁻² was not reported.49

Figure 7. Device architecture and chemical structures of materials employed.

Additional devices using a different stack consisting of ITO | NPB (HTL, 40nm) | mCBP (EBL, 10nm) | DiICzMes4: host X% (EML, 30nm) | T2T (HBL, 10nm) | T2T:LiQ 45% (EIL/ETL, 35nm) | Al (cathode, 100nm) were also fabricated. In these the concentration of the dopant was varied (5, 12, and 20 wt%) and different EML hosts additionally investigated: mCBP (hole transporting), DPEPO (electron transporting). Representative device performance and spectra are shown in Figure S37, with no significant improvement compared to the results in Figure 8. With increasing concentration no difference was observed in current density-voltage-luminance (JVL) and EQE as a function of current density although a broadening in the electroluminescence (EL) spectrum was observed. The broadening
is assigned to the dimer/excimer contribution as shown from the previous photophysical results (Figure S35d and Figure S36c).

In order to compensate for the low RISC rate of DiICzMes₄, we also applied it as a terminal emitter in hyperfluorescent OLEDs with a D-A-D TADF co-host. In order to ensure good spectral overlap necessary for energy transfer, we employed a dimethylacridine-tetramethylthioxanthene-S,S-dioxide (identified as TADF in Figure 7) based TADF previously reported to give high EQEs and deep blue emission [CIE of (0.15, 0.19)] in the same OLED stack.¹⁴ This D-A-D TADF was co-evaporated at 35% in the EML, alongside 1% DiICzMes₄ and bulk host DPEPO. The resulting OLEDs possessed good efficiency, with an EQEₘₐₓ>16% and CIE of (0.15, 0.11) enabled by triplet harvesting of the D-A-D co-host, while outputting narrow blue emission from the DiICzMes₄. The HF OLED showed relatively lower efficiency roll-off, offering a practical strategy to circumvent large efficiency roll-off resulting from inefficient k_{RISC} of the MR-TADF emitter (Figure 8).
Figure 8. OLED performance for different EMLs. (a) EL spectra of TADF D-A-D 35% (red), HF OLEDs 1:35 wt% (blue) in DPEPO host, absorption (black dotted) and PL (green) spectra of DiICzMes$_4$ 1 wt% in mCP for comparison. (b) CIE coordinates, where square (DiICzMes$_4$ only) and circle (HF) overlap, (c) JVL curves, and (d) EQE vs current density, where fitting has been applied (dotted line) to guide the reader.

As our integrating sphere system is not sensitive to very low luminances, we do not observe the same high maximum EQEs (~32%) previously reported using a similar hyperfluorescence approach with pICz.  However, comparing our device data at equivalent brightnesses reveals improved performance (Figure S38), which we infer is due to the improved efficiency roll-off of our D-A-D co-host. The previously reported DPAC-DtCzBN:PPF cohost has a similar intrinsic maximum efficiency as ours, and with slightly blue shifted EL spectrum should also enjoy marginally improved FRET overlap with
the MR-TADF emitter in the device. Despite the adequate FRET overlap in both devices, a subtle shoulder can still be observed in our EL spectra, indicating residual emission from the D-A-D co-host. As hyperfluorescence applications of MR-TADF emitters become increasingly popular to circumvent their low RISC rates,\textsuperscript{22,65-67} engineering both their PL spectra (for ideal-blue emission), as well as their absorption spectra (for minimal stokes shift, enabling broad compatibility with D-A-D TADF co-hosts)\textsuperscript{68} take on equally important roles for applications. The later of these can significantly alleviate the requirement for D-A-D co-hosts with deep blue EL, which remain challenging to design despite nearly a decade of intense global research in this direction.

We finally note that in both our hyperfluorescence devices and those previously reported, inclusion of the MR-TADF leads to significantly worse efficiencies at reasonable brightnesses compared to the D-A-D co-host alone. While the DiICzMes\textsubscript{4} would be expected to increase device performance due to spontaneously emitter dipole alignment and improved outcoupling\textsuperscript{47}, other detrimental processes must also be at play to result in an overall detriment to performance. These may include charge trapping or Dexter transfer to the slow-RISC MR-TADF dopant, although these processes have proven to be incredibly challenging to even quantify by traditional means.\textsuperscript{69} Therefore while the improvement in colour coordinate offered by the MR-TADF hyperfluorescence strategy is welcomed, it is clear that a deeper understanding of the relevant \textit{in operando} mechanism and processes is required to unlock their full potential.

**Conclusions**

We have designed and investigated an MR-TADF compound that does not contain any explicit electron-acceptor units, opening a new design paradigm for MR-TADF emitters. SCS-CC2 calculations guided the design, confirming a strategy to coincidentally decrease $\Delta E_{ST}$ and improve oscillator strength with increasing electronic delocalization. Photophysical measurements revealed a reduced $\Delta E_{ST}$ and increased $\Phi_{PL}$ were observed in both solution and doped films for DiICzMes\textsubscript{4} compared to ICz and
**ICzMes**. Although $\Delta E_{ST}$ was rather large at 0.26 eV in mCP, TADF was nonetheless observed in this and other solid-state hosts. Activation of TADF occurs through the involvement of higher-lying triplet states of different orbital types to $S_1$, resulting in non-negligible SOC.\textsuperscript{41, 42} Owing to inefficient RISC, simple guest-host OLEDs showed low efficiency, although hyperfluorescent devices achieved good $\text{EQE}_{\text{max}}$ of 16.5%, at deep-blue colour coordinates (0.15, 0.11) with improved relative efficiency roll-off. Discovery of new regions of chemical space suitable for the development of MR-TADF emitters thus opens new paths towards understanding their optical properties and improving their performance.

**Supporting Information**

$^1$H and $^{13}$C NMR, and HRMS spectra of all new compounds and HPLC traces of all the emitters; supplementary computational data and coordinates; supplementary photophysical data; supplementary device data; Crystallographic data for ICzMes, and DiICzMes.

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**References**


