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A three boron doped B/O/N multi-resonant TADF emitter for improved reverse intersystem crossing rate and efficient pure blue organic light-emitting diodes†

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Multiresonant thermally activated delayed fluorescence (MR-TADF) compounds exhibit significant potential as emitters in organic light-emitting diodes (OLEDs) due to their bright, narrowband emission, which provides a solution to the color saturation required by industry for ultra-high definition (UHD) displays. Here, we report the smallest three boron doped MR-TADF emitter (TBDON), a design that fuses two boron-contacting MR-TADF emitters, DOBNA and ADBNA-Me-Mes, together. The resulting emitter, TBDON, shows desirable narrowband pure blue emission ($\lambda_{PL}=472$ nm with FWHM = 28 nm) and efficient TADF with efficient reverse intersystem crossing (RISC), supported by a relatively fast k_{RISC} of 7.8 \times 10⁴ s⁻¹. The OLED with TBDON showed a high maximum external quantum efficiency (EQE_{max}) of 24.4%, an EQE of 17.2% at 100 cd m⁻², and Commission Internationale de l'Éclairage (CIE) coordinates of (0.14, 0.16). The ternary device employing DMAC-DPS as an assistant dopant showed improved performance with a higher EQE_{max} of 28.1% and milder efficiency roll-off with an EQE_{100/1000} of 24.4/17.5%. The high device performance demonstrates the promise of the proposed molecular design.

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Introduction

Organic light-emitting diodes (OLEDs) have now taken off as the privileged display technology across a range of consumer electronics categories, including smartwatches, mobile phones, and televisions, and are beginning to appear in an ever increasing number in the automotive sector. However, the external quantum efficiency (EQE) of blue subpixels remains suboptimal as the current materials rely on a triplet–triplet annihilation mechanism for exciton harvesting and thus the internal quantum efficiency is limited to 62.5%. Multiresonant thermally activated delayed fluorescence (MR-TADF) materials may provide a solution to this outstanding materials design

carbons (PAHs) typically containing both p- and n-dopants that are judiciously embedded to produce an alternating pattern of increasing and decreasing electron density in the excited state compared to the ground state. This is reflected in the shortrange charge transfer (SRCT) character of the lowest lying singlet and triplet excited states that lead to a moderately small singlet–triplet excited-state energy gap ($\Delta E_{\rm ST}$) that activates reverse intersystem crossing (RISC) channels and turns on TADF. 5.6 This ingenious molecular design endows MR-TADF emitters with a high photoluminescence quantum yield ($\Phi_{\rm PL}$), narrowband emission, and 100% exciton utilization efficiency, which make them highly attractive candidates for use in OLEDs.

challenge.4 These compounds are polycyclic aromatic hydro-

Since the first examples reported by Hatakeyama and coworkers, numerous blue emissive boron-containing MR-TADF OLED emitters (e.g., **DOBNA**, and **DABNA**, and **ADBNA-Me-Mes**) have been reported. However, due to their relatively large $\Delta E_{\rm ST}$ (\sim 0.20 eV), most emitters suffer from quite slow RISC ($k_{\rm RISC} < 10^4 \ {\rm s}^{-1}$), which leads to undesirably severe efficiency roll-off. Extending the MR-TADF-skeleton to include multidoped boron/nitrogen atoms can facilitate a more delocalized SRCT excited state, leading to smaller $\Delta E_{\rm ST}$, thereby accelerating the RISC process. Hatakeyama et~al. first introduced this extended design strategy in 2018, wherein they altered the number of boron atoms across the emitters **B2** and **B3** (Fig. S10†). By increasing the number of embedded boron atoms

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from two to three, $\Delta E_{\rm ST}$ values for **B2** and **B3** decreased from

0.19 to 0.15 eV, respectively, in 1 wt% doped films in 3,3'-di(9H-

embedded boron atoms increasing from four to eight (for example, CzB4-oPh, Fig. S10†), leading to progressively smaller $\Delta E_{\rm ST}$ values from 0.04 to 0.03 eV and faster $k_{\rm RISC}$ from 6.4 to 65.0 \times 10⁴ s⁻¹, respectively.²⁴

carbazol-9-yl)-1,1'-biphenyl (mCBP).15 The linear two boron embedded MR-TADF emitter v-DABNA (Fig. S10†) was subsequently reported by the same group, which showed a much Although these elegant designs demonstrate that k_{RISC} can smaller $\Delta E_{\rm ST}$ (0.02 eV) and faster $k_{\rm RISC}$ (2.0 \times 10⁵ s⁻¹) in 1 wt% be improved to $>10^5$ s⁻¹, most of these compounds emit in the doped films in DOBNA-OAr compared to DABNA-1 (Fig. S10†), sky-blue-to-green region. By constructing twisted-boron-/ with a $\Delta E_{\rm ST}$ of 0.20 eV and a $k_{\rm RISC}$ of 9.9 \times 10³ s⁻¹ in 1 wt% nitrogen-/oxygen-embedded fused-ring frameworks, Yang et al. doped films in mCBP.8,16 This work directly supports the reported a series of deep blue MR-TADF emitters with the hypothesis that having an extended π -network is necessary for number of boron atoms increasing from two to four, leading to MR-TADF compounds having a relatively smaller $\Delta E_{\rm ST}$ and progressively smaller $\Delta E_{\rm ST}$ values from 0.17 to 0.09 eV and faster $k_{\rm RISC}$ from 8 to 30 imes 10⁴ s⁻¹.²⁵ By incorporating the ultraviolet faster k_{RISC} . There are now numerous examples of two-boronembedded MR-TADF emitters with small $\Delta E_{\rm ST}$ < 150 meV and emissive **DOBNA** motif within a π -extended MR-TADF skeleton, $k_{\rm RISC} \ge 10^5 {\rm \ s^{-1}} \ (e.g., {\rm \ BOBS-Z}, ^{17} {\rm \ BN3}, ^{18} {\rm \ and \ TPD4PA}^{19}).$ However, our group has reported a series of deep blue emitters and examples of MR-TADF emitters incorporating three or more devices. For instance, MesB-DIDOBNA-N26 emits at 402 nm and boron atoms into the PAH skeleton are far fewer in number and has a $\Phi_{\rm PL}$ of 75% but has only a moderate $k_{\rm RISC}$ of 9.8 \times 10³ s⁻¹ and large ΔE_{ST} of 0.24 eV in a 1.5 wt% doped film in diphenyl[4this is hypothesized to lead to even more efficient RISC. Hatakeyama et al. reported a π -extended helical MR-TADF emitter, V-(triphenylsilyl)phenyl]phosphine oxide (TSPO1) The OLED with **DABNA-Mes**, ²⁰ which has a k_{RISC} of 4.4×10^5 s⁻¹ in 1 wt% doped MesB-DIDOBNA-N showed an EQE $_{max}$ of 16.2% and had a CIE $_{\nu}$ films in poly(methylmethacrylate) (PMMA). This translated to coordinate of 0.049. The related four-boron embedded MRan efficient solution-processed OLED emitting at a λ_{EL} of TADF emitter **NOBNacene** has a slower k_{RISC} of 3.7 \times 10³ s⁻¹ 480 nm, with corresponding CIE coordinates of (0.09, 0.21), and as a 1.5 wt% doped film in TSPO1. The OLED with NOBNacene²⁷ showing an EQEmax of 22.9%. The same group developed showed an EQE_{max} of 11.2% at CIE coordinates of (0.18, 0.07). To improve the $k_{\rm RISC}$, we developed the V-shaped MR-TADF a three-boron-containing MR-TADF emitter ω -DABNA²¹ showing a fast k_{RISC} of 1.2 \times 10⁵ s⁻¹. Our group also reported emitter **f-DOABNA**, ²⁸ which shows a much faster k_{RISC} of 2 \times two three-boron-containing linear MR-TADF heptacene 10^6 s^{-1} and high Φ_{PL} of 90% in 1 wt% doped films in **DOBNA**-Tol (Fig. S10†). This translated to high performance OLEDs in 1 systems, α -3BNOH and α -3BNMes, which show a large ΔE_{ST} of 0.28 eV for each, thus resulting in a low $k_{\text{RISC}} < 10^3 \text{ s}^{-1}$ in 1 wt% wt% doped films in 1,3-bis(N-carbazolyl)benzene (mCP) with an doped films in poly(methyl)methacrylate (PMMA).22,23 Hata-EQE_{max} of 19.5% and CIE coordinates of (0.15, 0.04); however, keyama and co-workers subsequently reported a series of efficient roll-off remains problematic with an EQE_{100/1000} of extended heptadecacene frameworks with the number of 15.9/7.5%. Using a similar backbone structure, Hatakeyama

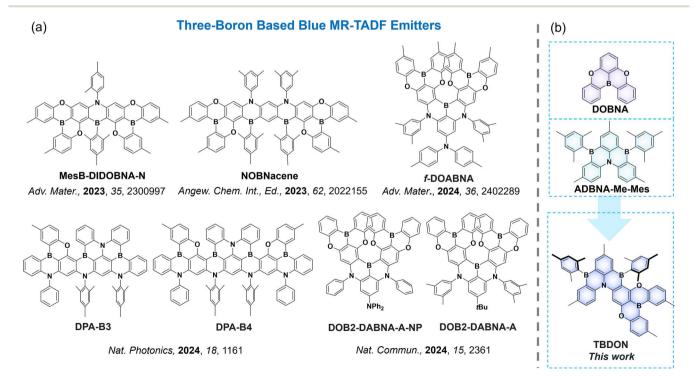


Fig. 1 (a) Chemical structures of three boron-based blue MR-TADF compounds and (b) the design strategy of TBDON.

and co-workers reported the deep blue emitter **DOB2-DABNA-A**, which shows a similarly fast $k_{\rm RISC}$ of $1.1 \times 10^6~{\rm s}^{-1}$ and high $\Phi_{\rm PL}$ of 92% in 1 wt% doped films in PMMA.²⁹ The device showed an EQE_{max/100/1000} of 22.8/23.3/21.6% and CIE coordinates of (0.14, 0.05). These examples illustrate that certain multi-boron systems containing the **DOBNA** skeleton can show significant potential as emitters for deep-blue and stable devices (Fig. 1).

ADBNA-Me-Mes is arguably the smallest MR-TADF emitter containing two boron atoms embedded within a PAH skeleton. This compound shows sky-blue emission peaking at a λ_{PL} of 482 nm and a resistance to aggregation due to the presence of the bulky mesityl group.9 With the objective of designing an emitter with a faster k_{RISC} and showing pure blue emission (CIE_x + CIE_{ν} < 0.3), we merged the motifs of **ADBNA-Me-Mes** with DOBNA into a single molecule, TBDON, a three-boroncontaining MR-TADF emitter. In toluene, TBDON exhibits pure blue emissions at a λ_{PL} of 462 nm, a value that is intermediate between those of **ADBNA-Me-Mes** ($\lambda_{PL} = 482 \text{ nm}$) and **DOBNA** (λ_{PL} of 398 nm). **TBDON** has a comparable Φ_{PL} of 88%, a shorter delayed lifetime, $\tau_{d,avg}$, of 35.6 μs , and a narrower emission profile (FWHM of 28 nm) compared to these two reference compounds. Its k_{RISC} of 7.8 \times 10⁴ s⁻¹ in 3 wt% doped 2,6-bis[3-(9H-carbazol-9-yl)phenyl]pyridine DCzPPy) is ten times faster than those of **ADBNA-Me-Mes** ($\Phi_{\rm PL} =$ 89%, $\tau_{\rm d} = 165~\mu {\rm s}$, FWHM = 33 nm and $k_{\rm RISC} = 7.6 \times 10^3~{\rm s}^{-1}$ in 1 wt% doped films in DOBNA-OAr). The device with 4 wt% TBDON in 2,6-DCzPPy showed narrowband blue electroluminescence at a λ_{EL} of 471 nm and FWHM of 29 nm, leading to CIE coordinates of (0.12, 0.16). The device showed a relatively mild efficiency roll-off, with an EQE $_{max/100/1000}$ of 24.4/20.2/13.7%. To improve the device performance further, ternary devices containing the assistant dopant 10,10'-(4,4'-sulfonylbis(4,1phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (**DMAC-DPS**) were fabricated, which showed an EQE $_{\rm max}$ of 28.1% and a suppressed efficiency roll-off, with an EQE $_{\rm 100/1000}$ of 24.4/17.5%.

Results and discussion

TBDON was synthesized following a two-step linear reaction sequence (Fig. 2a). DOB-Br was synthesized according to a previously reported protocol.27 DOB-DPA was obtained in a yield of 85% through a palladium-catalyzed Buchwald-Hartwig coupling between **DOB-Br** and 4,4'-dimethyldiphenylamine. Electrophilic borylation of DOB-DPA with BBr₃ and quenching with 2-mesitylmagnesium bromide afforded the desired product TBDON in 16% yield; the low yield is attributed to the challenging purification, due to similar R_f (retention factor) values between TBDON and the impurities; the sample could only be obtained by recrystallization from toluene and ethanol following chromatography. The structure and purity of TBDON were confirmed by ¹H and ¹³C NMR spectroscopy, highresolution mass spectrometry (HRMS), single crystal X-ray diffraction (SC XRD) analysis, high performance gel permeation chromatography (GPC), and elemental analysis (Fig. S1-S8†). The thermal stability of TBDON was investigated by thermogravimetric analysis (TGA) (Fig. S15†). This compound is thermally stable, with a 5% mass loss ($T_{\rm d}$) occurring at 374 °C.

Single crystals of **TBDON** (CCDC: 2431387) were obtained by slow diffusion of EtOH vapors into a saturated solution of **TBDON** in toluene over several days. The crystal structure is shown in Fig. 2b. No intermolecular hydrogen bonding or π - π stacking interactions exist in the crystal structure. **TBDON** adopts a twisted geometry, with a dihedral angle of 53.48(9)°

Fig. 2 (a) Synthesis route of target TBDON. (b) Single crystal structure of TBDON and its side view. Thermal ellipsoids are displayed at the 50% probability level; solvent is omitted for clarity.

between the DOBNA unit and an adjacent phenyl ring (Fig. S9†). The two mesityl moieties are oriented approximately orthogonal to the adjacent rings (angles of 73.89(12) and $84.67(12)^{\circ}$). All these structural features endow **TBDON** with a resistance to aggregation in the crystalline state.

Theoretical calculations were carried out to provide insight into the optoelectronic properties of **TBDON**. The geometry in the ground state was first optimized using Density Functional Theory at the PBE0/6-31G(d,p) level based on a structure generated from Chem3D, which has a similar geometry to that found in the crystal structure. The HOMO is distributed over the whole molecular skeleton, while the LUMO is mainly localized on the ADBNA-Me-Mes portion of the emitter (Fig. 3a). The calculated HOMO and LUMO levels are -5.59/-1.83 eV, which are essentially the same as those of ADBNA-Me-Mes (-5.61/-1.84 eV, Fig. S13a†). There is a small geometric change in the S₁ state compared to the ground state, with a RMSD of 0.14 Å (Fig. S11†), which indicates that the emission is likely to be narrowband. Excited-state calculations were performed at the SCS-ADC(2)/cc-pVDZ level, which we have previously shown to accurately predict $\Delta E_{\rm ST}$ in MR-TADF emitters.³⁰ The calculated S_1/T_1 energies of **TBDON** are 3.06/2.96 eV, which are slightly higher than those of ADBNA-Me-Mes at 2.81/2.64 eV, implying that the emission should be blue-shifted in the former. Notably, the $\Delta E_{\rm ST}$ of 0.10 eV is smaller than the 0.17 eV predicted for ADBNA-Me-Mes, attributed to the more separated FMOs in the former, as shown in Fig. 3a and S13b.† There is an expected alternating pattern of increasing and decreasing electron density in the S₁, S₂, T₁ and T₂ states compared to the ground state that is indicative that these states have SRCT character (Fig. 3b). The difference density plots of the S₁ and T₁ states

reveal that the electron density is mainly located on the **ADBNA-Me-Mes** part of the molecule (Fig. S13b†), which is similar to the spin-density distribution (SSD) of the T_1 state of **TBDON** (Fig. S12†), indicating that S_1 and T_1 each have similar character to those of **ADBNA-Me-Mes**. The difference density plots of the S_2 and T_2 states are mainly located on the **DOBNA** fragment. DFT calculations predict a small SOC matrix element (SOCME) of 0.067 cm⁻¹ between S_1 and T_1 at the optimized T_1 geometry, which is slightly smaller than that (0.099 cm⁻¹) of **ADBNA-Me-Mes** (Fig. S13c†). While **TBDON** shows a smaller SOCME between S_1 and T_1 , the closely lying T_2 and T_3 states have a much larger SOC to S_1 (0.291 and 0.621 cm⁻¹, respectively), reflecting the significant differences in orbital types between these excited states (Fig. 3c). These calculations suggest that faster RISC proceeds *via* T_2/T_3 to S_1 for **TBDON**.³¹

Inferences from the electrochemistry can provide an indication of the energies of the FMOs. As such, the electrochemical properties of **TBDON** were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in deaerated DCM with 0.1 M tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte (Fig. S16 and Table S2 \dagger). The CV reveals that the oxidation and reduction processes are irreversible. The oxidation and reduction potentials, $E_{\rm ox}$ and $E_{\rm red}$, determined, respectively, from the first oxidation and reduction peaks of the DPV, are 1.33 and -1.73 V ν s. the saturated calomel electrode (SCE), while the redox gap, ΔE , is 3.06 V. The corresponding HOMO and LUMO energies are -5.67 and -2.61 eV.

We next investigated the photophysical properties of the monomolecular species of **TBDON** in dilute toluene solution (10⁻⁵ M). The UV/visible absorption spectrum (Fig. 4a) shows intense bands peaking at a λ_{abs} of 339 (molar absorptivity, ε , of

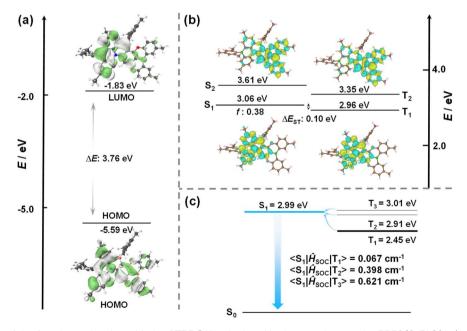
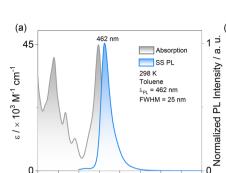


Fig. 3 (a) Distributions of the frontier molecular orbitals of TBDON, calculated in the gas phase at the PBE0/6-31G(d,p) level (isovalue: 0.02). (b) Difference density plots of S_1/S_2 and T_1/T_2 excited states (calculated in the gas phase at the SCS-ADC(2)/cc-pVDZ level) for TBDON (isovalue: 0.02). f is the oscillator strength. (c) Spin-orbit coupling matrix element (SOCME) for TBDON based on the optimized T_1 geometry at the uPBE0/6-31G(d,p) level.

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500

Wavelength / nm

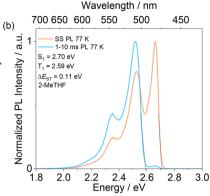


Fig. 4 (a) Absorption and steady-state PL (SS PL) spectra in toluene at room temperature ($\lambda_{exc} = 340$ nm); (b) SS PL and time-gated PL (1–10 ms) emission spectra after Jacobian transformation measured in 2-MeTHF glass at 77 K ($\lambda_{exc} = 340$ nm).

 $40.4 \times 10^3~\text{M}^{-1}~\text{cm}^{-1}$) and 366 nm ($20.5 \times 10^3~\text{M}^{-1}~\text{cm}^{-1}$). The bands ranging from 300 to 380 nm are attributed to π - π^* transitions localized over the whole skeleton, assigned from the TD-DFT calculations (Fig. S14†). The lower energy bands peaking at 390 nm are attributed to transitions localized on the **DOBNA** unit given the similar wavelength to the low energy band of *tBuDOBNA* ($\lambda_{abs} = 383~\text{nm}$).³² The intense absorption band peaking at a λ_{abs} of 448 nm ($\varepsilon = 44.9 \times 10^3~\text{M}^{-1}~\text{cm}^{-1}$) corresponds to the SRCT transition associated with the **ADBNA** unit, which is blue-shifted compared to the SRCT absorption band ($\lambda_{abs} = 458~\text{nm}$) of **ADBNA-Me-Mes** in DCM.⁹

300

The photoluminescence (PL) spectrum of **TBDON** in toluene is narrowband (FWHM of 25 nm), peaking desirably at a λ_{PL} of 462 nm. The λ_{PL} of **TBDON** is intermediate to those of **ADBNA-Me-Mes** (λ_{PL} of 482 nm) and **DOBNA** (λ_{PL} of 398 nm) in DCM.⁷ There is also a small Stokes shift of 24 nm (Fig. 4a); this and the narrowband emission reflect the rigid nature of this emitter. There is modest positive solvatochromism of the PL (Fig. S17†), which is consistent with the emissive excited state of SRCT character classifying this compound as an MR-TADF emitter.

The S_1/T_1 energies, determined from the onsets of the prompt fluorescence and phosphorescence spectra at 77 K in 2-MeTHF glass, are 2.70 and 2.59 eV (Fig. 4b). The corresponding ΔE_{ST} , calculated from the difference in energy between these two states, is 0.11 eV, which matches the ADC(2) calculated value of 0.10 eV. The steady-state PL spectra and time-resolved PL decays in aerated toluene show that there is partial quenching of the emission due to O_2 (Fig. S18†); indeed, the Φ_{PL} decreases from 84 to 68% upon exposure to air. The prompt and

delayed emission lifetimes, $\tau_{\rm p}$ and $\tau_{\rm d,avg}$, in degassed toluene solution are 4.2 ns and 13.2 µs, respectively. Rate constants for the various kinetics processes are summarized in Table S3† and the rate constant for reverse intersystem crossing, $k_{\rm RISC}$, is 5.6 × $10^4~{\rm s}^{-1}$. All these results indicate that **TBDON** in toluene solution emits *via* TADF.

With the goal of employing TBDON as an emitter in OLEDs, we next investigated its photophysical properties in doped films. After a doping concentration screening study in mCP (E_{T} = 2.81 eV),33 which identified 3 wt% doping as optimal, and a targeted host screen (Fig. S19 and S20†), we identified 2,6-DCzPPy as the best host. We thus investigated in more detail the photophysics of TBDON in this host (Table 1). In 3 wt% doped films in 2,6-DCzPPy, TBDON shows narrowband blue emission at a λ_{PL} of 472 nm (FWHM of 28 nm), which is slightly redshifted compared to that in toluene. This emission, however, is blue-shifted and more narrowband compared to the emission of **ADBNA-Me-Mes** in DOBNA-OAr host ($\lambda_{PL} = 482 \text{ nm}$; FWHM = 33 nm).9 The SS PL intensity in air is lower than that seen under vacuum, indicating that there are likely triplet excitons being quenched. The S₁/T₁ energies, determined from the onsets of the SS PL and delayed emission spectra at 77 K (Fig. S21†), are 2.69/2.57 eV, respectively, with a corresponding $\Delta E_{\rm ST}$ of 0.12 eV. This value is almost identical to the value in 2-MeTHF and smaller than the ΔE_{ST} values of **ADBNA-Me-Mes** (0.18 eV in 1 wt% doped films in DOBNA-OAr) and DOBNA (0.18 eV in 1 wt% doped films in PMMA). 9,34 The activation energy $\Delta E_{\rm a}^{\rm TADF}$ is estimated to be 60 meV (Fig. S22†). The small activation energy in 2,6-DCzPPy may indicate the involvement of higher-lying

Table 1 Photophysical data of TBDON in doped films in 2,6-DCzPPy

Emitters	$\Phi_{\mathrm{PL}}{}^a/\%$	$\lambda_{\mathrm{PL}}{}^{b}/\mathrm{nm}$	FWHM ^c /nm	S ₁ ^d /eV	T ₁ ^e /eV	$\Delta E_{\rm ST}^f/{\rm eV}$	$\tau_{\mathrm{p}}^{\ g}/\mathrm{ns}$	$\tau_{\mathrm{d,avg}}^{}h}/\mu\mathrm{s}$	$k_{\rm RISC}^{i}/10^{4} {\rm s}^{-1}$
TBDON	88	472	28	2.69	2.57	0.12	4.0	35.6	7.8
ADBNA-Me-Mes ⁹	89	482	33	_	_	0.18	6.0	165	0.76

^a Measured using an integrating sphere under nitrogen ($\lambda_{\rm exc}=340$ nm). ^b Obtained at 298 K, $\lambda_{\rm exc}=340$ nm. ^c Full-width at half-maximum. ^d Obtained from the onset of the delayed emission spectrum (1–10 ms) at 77 K ($\lambda_{\rm exc}=340$ nm). ^f $\Delta E_{\rm ST}=E$ (S₁) – E (T₁). ^g Measured at 300 K under vacuum by time-correlated single photon counting (TCSPC). ^h Measured at 300 K under vacuum by MCS, $\lambda_{\rm exc}=379$ nm. ⁱ The calculation methodology is described in the ESI and data are provided in Table S3.³⁵

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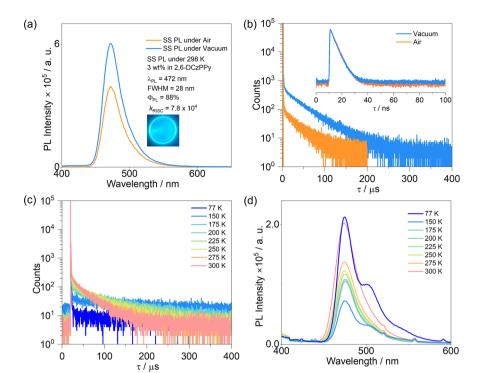


Fig. 5 (a) Comparison of the intensity of the PL spectra under vacuum and in air ($\lambda_{exc} = 340$ nm); (b) time-resolved PL decays ($\lambda_{exc} = 379$ nm) in 3 wt% 2,6-DCzPPy doped films. Temperature-dependent (c) TR PL decay ($\lambda_{exc} = 379$ nm) and (d) SS PL spectra ($\lambda_{exc} = 340$ nm) of 3 wt% TBDON in 2,6-DCzPPy.

triplet excited states in the RISC process. The time-resolved PL (TR-PL) decay shows obvious prompt and delayed components, implicating TADF. Under vacuum, the prompt PL decays with a lifetime, τ_p , of 4.0 ns and the delayed PL decays with a lifetime, $\tau_{\rm d,avg}$, of 35.6 µs. The prompt lifetime is almost identical to the value in toluene solution, while the $\tau_{d,avg}$ is much longer, indicating that non-radiative decay is suppressed in the doped film. Notably, the $\tau_{\rm d,avg}$ of the 3 wt% doped film of TBDON in 2,6-DCzPPy is much shorter than that of the 1 wt% doped film of ADBNA-Me-Mes in DOBNA-OAr ($\tau_{d,avg}$, of 165 µs), arising from the smaller $\Delta E_{\rm ST}$ in the former. The excited-state kinetics were determined based on the measured Φ_{PL} and lifetimes (Table S3†). The $k_{\rm RISC}$ of 7.8 \times 10⁴ s⁻¹ for **TBDON** is over 10 times faster than that of ADBNA-Me-Mes $(7.6 \times 10^3 \text{ s}^{-1})$, indicating that there is a more efficient upconversion of triplet excitons to singlets in TBDON, benefitting from its shorter $\tau_{d,avg}$. Temperature-dependent SS PL and TR PL measurements demonstrate that an increase in the delayed emission is responsible for the increase in intensity of the PL as the temperature increases (Fig. 5c and d).

The excellent photophysical performance of **TBDON** encouraged us to evaluate this compound as an emitter in vacuum-deposited OLEDs. Based on prior work fabricating blue OLEDs we used the following device structure: 32 ITO/HATCN (5 nm)/TAPC (30 nm)/TCTA (10 nm)/mCP (5 nm)/2,6-DCzPPy:**TB-DON** (x wt%) (20 nm)/TmPyPB (40 nm) LiF (1 nm)/Al (100 nm), where indium tin oxide (ITO) is the anode, 1,4,5,8,9,11-hex-azzatriphenylenehexacarbonitrile (HATCN) is the hole injection layer, both 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)

benzenamine] (TAPC) and tris(4-carbazoyl-9-ylphenyl)amine (TCTA) act as hole transporting layers, mCP acts as an exciton blocking layer, 1,3,5-tri(*m*-pyridin-3-ylphenyl)benzene (TmPyPB) is the electron transporting material, and LiF modifies the work function of the aluminum cathode. The chemical structures of these materials are shown in Fig. S23,† the device performance is summarized in Fig. 6 and S25† and the data are collated in Table 2 and S4†.

Due to the differing film preparation methods between the photophysical studies and the devices, we fabricated devices using different doping concentrations of TBDON in the emissive layer, ranging from 2 to 5 wt%, (Fig. S25†). All the devices show maximum external quantum efficiencies, EQEmax, of more than 20%. With increasing emitter doping concentrations from 2 to 5 wt%, the efficiency roll-off decreased, ostensibly due to an improved charge mobility balance. The devices show narrowband blue emission across the range of emitter doping concentrations investigated, with λ_{EL} at around 470 nm, and corresponding CIE coordinates of (0.12, 0.15). These devices are blue-shifted compared to those employing ADBNA-Me-Tip and **ADBNA-Me-Mes** [λ_{EL} of 481 and 480 nm and CIE coordinates of (0.10, 0.27) and (0.11, 0.29), respectively]. The highest EQE_{max} of 24.4% was achieved with 4 wt% TBDON, with an associated color point characterized by a λ_{EL} of 471 nm, an FWHM of 29 nm and CIE coordinates of (0.12, 0.16). Gratifyingly, compared to the rather severe efficiency roll-off in the devices with ADBNA-based emitters (EQE_{max}/EQE₁₀₀ = 16.2/11.1% and 21.4/15.4% for the devices with ADBNA-Me-Tip and ADBNA-Me-Mes, respectively), the devices with TBDON showed milder

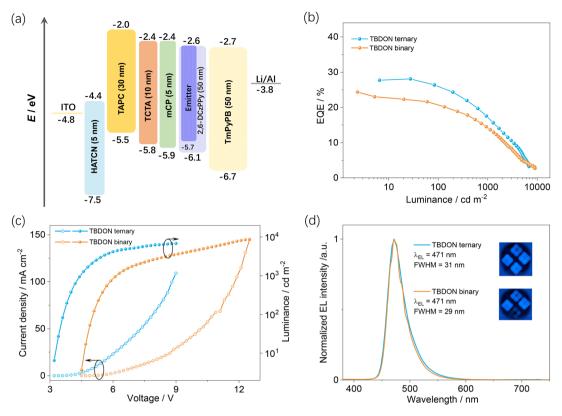


Fig. 6 (a) Device configuration and energy levels for each layer; (b) EQE *versus* electroluminescence characteristics. (c) J-V-L characteristics; (d) electroluminescence spectra for devices; inset: images of working devices.

Table 2 Data of devices with binary and ternary emissive layers

Device	$V_{\rm on}^{a}/{\rm V}$	$\lambda_{\rm EL}/nm$	FWHM ^b /nm	CIE	$\mathrm{EQE}_{\mathrm{max/100/1000}}^{c}/\%$	$L_{\rm max}^{d}/{\rm cd}~{\rm m}^{-2}$
ADBNA-Me-Mes ⁹ TBDON (binary) TBDON (ternary)		481	32	(0.10, 0.27)	16.2/11.1/—	<1000
	4.3	471	29	(0.12, 0.16)	24.4/20.2/13.7	8800
	3.2	471	30	(0.12, 0.17)	28.1/24.4/17.5	6800

 $[^]a$ Turn on voltage, recorded at 1 cd m $^{-2}$. b Full width at half-maximum of the electroluminescence spectrum. c Maximum external quantum efficiency/EQE at 100 cd m $^{-2}$ /EQE at 1000 cd m $^{-2}$. d Maximum luminance.

efficiency roll-off, with an EQE $_{100}$ of 20.2% and EQE $_{1000}$ of 13.7%, respectively, which is attributed to the faster $k_{\rm RISC}$ from **TBDON**.

In an effort to improve the device performance, we opted to explore a ternary emissive layer architecture where an assistant dopant would serve to more efficiently harvest excitons and then transfer these to **TBDON**, acting as the terminal emitter. Based on an analysis of the spectral overlap between potential TADF emitters and the absorption of **TBDON**, we identified **DMAC-DPS** as a suitable assistant dopant capable of efficiently engaging in Förster resonance energy transfer (FRET) with **TBDON** (Fig. S26†). The faster $k_{\rm RISC}$ of 1.8×10^5 s $^{-1}$ from the 10 wt% doped film of **DMAC-DPS** in mCP³⁶ should contribute to reducing the efficiency roll-off in the device. Ternary devices were fabricated by incorporating 20 wt% **DMAC-DPS** as the assistant dopant into the EML and 2 wt% of **TBDON** as the terminal emitter (Fig. 6). Employing the system of **TBDON**:

DMAC-DPS: 2,6-DCzPPy = 2/20/78% as the EML produced devices showing an improved EQEmax of 28.1% and alleviated efficiency roll-off, with an EQE₁₀₀ and EQE₁₀₀₀ of 24.4 and 17.5%, respectively (Fig. 6b). Unfortunately, despite the higher device efficiencies, the efficiency roll-off was not significantly improved. To understand the origin of this surprising result, we explored the photophysical properties of spin-coated films emulating this ternary EML (Fig. S27†). The ternary film has a slightly lower $\Phi_{\rm PL}$ of 82% (88% for the binary film) and an almost identical SS PL spectrum to the binary film (Fig. S27a†), indicating that there is efficient energy transfer from DPS-**DMAC** to **TBDON**. However, the $\tau_{d,avg}$ of the ternary film remains effectively unchanged, with a slightly shorter $\tau_{d,avg}$ of 31.5 µs (Fig. S27b†), compared to 35.6 µs for the binary film, leading to a similar k_{RISC} of 6.34 \times 10⁴ s⁻¹ (Table S3†), indicating that TBDON remains engaged in the triplet exciton upconversion process. However, the figure of merit for TADF emitters $k_{\rm r}^{\rm S}K_{\rm eq}$ of the ternary film is higher at 3.6 \times 10⁴ s⁻¹ compared to 3.3 \times 10⁴ s⁻¹ for the binary film, indicating more efficient exciton harvesting in the ternary system, which explains the lower efficiency roll-off.

Conclusions

Here, we have developed a tri-boron based MR-TADF emitter (TBDON) by fusing MeDOBNA and ADBNA-Me-Mes together. TBDON emits desirably at an intermediate pure blue emission ($\lambda_{\rm PL}$ of 472 nm) between the sky blue of ADBNA-Me-Mes and the purple of DOBNA. TBDON has a high $\Phi_{\rm PL}$ of 88%, moderate $\Delta E_{\rm ST}$ values of 0.12 eV, and shorter delayed lifetimes of 35.6 µs in 3 wt% doped films in 2,6-DCzPPy. OLEDs using this emitter showed efficient performance with an EQE_{max} of 24.4%, relatively mild efficiency roll-off (EQE_{100/1000} = 20.2/13.7%), and narrowband blue emission peaking at 471 nm, with CIE coordinates of (0.12, 0.16). To further optimize the device performance, the D-A TADF emitter, DMAC-DPS, was employed as an assistant dopant in a ternary device configuration. These devices showed a higher EQE_{max} of 28.1%, without adversely affecting the color purity.

Data availability

The research data supporting this publication can be accessed at https://doi.org/10.17630/e2d9724d-fe70-4034-9441-e20db3dfcbf8. The X-ray structural data can be obtained from the Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/structures) as deposition number 2431387.

Author contributions

Sen Wu and Dongyang Chen contribute equally to this paper. Sen Wu: conceptualization, investigation, writing – original draft preparation, review & editing. Dongyang Chen: investigation for devices, review & editing. Mathilde Seinfeld: part of synthesis, review & editing. Aidan P. McKay and David B. Cordes: crystal analysis, review & editing. Xiaohong Zhang: resources, review & editing. Eli Zysman-Colman: project management, supervision, resources, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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