

# A Deep Blue Heteroatom Doped Nonacene That Exhibits Multi-Resonant Thermally Activated Delayed Fluorescence and its Use as an Emitter in High-Performance Deep Blue Organic Light-Emitting Diodes

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## Abstract

We present a p- and n-doped nonacene compound, **NOBNacene**, that represents a rare example of a linearly extended ladder-type multiresonant thermally activated delayed fluorescence (MR-TADF) emitter. This compound shows efficient narrow deep blue emission ( $\lambda_{\text{PL}} = 410$  nm, FWHM = 38 nm,  $\Phi_{\text{PL}} = 71\%$ ,  $\tau_{\text{d}} = 1.18$  ms) in 1.5 wt% TSPO1 thin film. The organic light-emitting diode (OLED) using this compound as the emitter shows a comparable electroluminescence spectrum ( $\lambda_{\text{EL}} = 409$  nm, FWHM = 37 nm) and a maximum external quantum efficiency ( $\text{EQE}_{\text{max}}$ ) of 8.5% at CIE coordinates of (0.173, 0.055). The  $\text{EQE}_{\text{max}}$  values were increased to 11.2% at 3 wt% doping of the emitter within the emissive layer of the device. At this concentration, the electroluminescence spectrum broadened slightly, leading to CIE coordinates of (0.176, 0.068).

## Introduction

The performance of organic light-emitting diodes (OLEDs) has advanced significantly since the first OLED developed by Tang and Van Slyke more than 30 years ago.<sup>1,2</sup> OLED technology is now widely adopted in a range of consumer electronics such as mobile phones, smart watches, and televisions. Singlet and triplet excitons are formed in an electroluminescent (EL) device in the ratio 1:3 due to the Fermionic nature of holes and electrons.<sup>3</sup> Commercial displays use two classes of emitters for the primary colors.<sup>2</sup> Phosphorescent emitters are used for green and red, whereas triplet-triplet annihilation (TTA) using purely organic emitters are used for the blue emitter as there is at present not a sufficiently stable blue phosphorescent OLED.<sup>4</sup> OLEDs with TTA emitters, however, can only achieve a maximum 62.5% internal quantum efficiency (IQE), thus, there is still room for improvement of the overall efficiency of the device. Not surprisingly, there is a huge effort undertaken by both academia and industry to develop stable and high efficiency blue emitters that can harvest 100% IQE in the device.<sup>4</sup> Furthermore, deep blue OLED light sources can find application beyond displays,<sup>5</sup> such as for sterilization,<sup>6</sup> and dental<sup>7</sup> and dermatological treatments.<sup>8</sup> Purely organic thermally activated delayed fluorescent (TADF) emitters provide a tantalizing solution as TADF OLEDs can achieve up to 100% IQE.<sup>9</sup> However, donor-acceptor (D-A) TADF compounds show very broad emission due to the long-range charge-transfer (LRCT) character of the excited state and the broad range of accessible geometries in the excited state as the D and A units are connected through single bonds.<sup>10</sup> This results in OLEDs that show poor color purity.<sup>11</sup> A solution to this apparent weakness of D-A TADF emitters was advanced by Hatakeyama *et al.* who demonstrated how p- and n-doped nanographenes, termed multi-resonant TADF (MR-TADF) emitters, could also exhibit TADF but with much narrower emission profiles.<sup>12</sup> The narrow emission spectra were rationalized in terms of the rigid structure of these compounds together with the short-range charge transfer (SRCT) nature of the emissive excited state.<sup>10</sup>

The potential of MR-TADF compounds to act as pure blue OLED emitters was first exemplified by the DABNA series (Figure 1).<sup>12</sup> **DABNA-1** presents a photoluminescence maximum,  $\lambda_{\text{PL}}$ , of 460 nm, a full width at half maximum, FWHM, of 30 nm, a high photoluminescence quantum yield,  $\Phi_{\text{PL}}$ , of 88%, and

a moderate singlet-triplet energy gap,  $\Delta E_{ST}$ , of 180 meV in 1 wt% mCBP host. The corresponding OLED showed pure blue emission at moderate efficiency ( $\lambda_{EL} = 460$  nm, FWHM = 30 nm,  $E_{QE_{max}} = 13.5\%$ ,  $CIE_Y = 0.09$ ). The same group reported a  $\pi$ -extended version of **DABNA-1**,  **$\nu$ -DABNA**, which still represents the pinnacle of blue MR-TADF emitter design.<sup>13</sup> This emitter exhibited efficient narrowband blue emission ( $\lambda_{PL} = 467$  nm, FWHM = 18 nm,  $\Phi_{PL} = 90\%$ ) and a very small  $\Delta E_{ST}$  of 17 meV in 1 wt% DOBNA-OAr host. The OLED showed an impressive performance with an  $E_{QE_{max}}$  as high as 34.4% at  $\lambda_{EL}$  of 469 nm, a FWHM of 18 nm and CIE coordinates of (0.12, 0.11). Indeed, compared to the OLED with **DABNA-1**, there is a remarkable improvement in the device performance with  **$\nu$ -DABNA**. The same group modified the structure of  **$\nu$ -DABNA** by replacing one of the nitrogen atoms with a less electron-donating oxygen atom as in  **$\nu$ -DABNA-OMe**.<sup>14</sup> This emitter maintained efficient and narrowband blue emission ( $\lambda_{PL} = 464$  nm, FWHM = 24 nm in 1 wt% DABNA-OAr). The OLED with this derivative showed a slightly blue-shifted EL of 465 nm (FWHM = 23 nm,  $E_{QE_{max}} = 29.5\%$ ). Kwon *et al.* modified the  **$\nu$ -DABNA** core to incorporate methyl and electron-withdrawing fluorine substituents.<sup>15</sup> Among their three emitters, **4F-*m*- $\nu$ -DABNA** ( $\lambda_{PL} = 455$  nm, FWHM = 14 nm in PhMe) exhibited the most hypsochromic emission compared to the parent  **$\nu$ -DABNA** ( $\lambda_{PL} = 467$  nm, 1 wt% doped in DABNA-OAr).<sup>16</sup> OLEDs with **4F-*m*- $\nu$ -DABNA** showed  $E_{QE_{max}}$  of 33.7% and an impressive CIE coordinate of (0.13, 0.06).<sup>15</sup> Yasuda *et al.* investigated doping mixed donor (oxygen and sulfur) atoms within the  **$\nu$ -DABNA** core to tune the emission into the deep blue region.<sup>17</sup> The new emitters all presented blue-shifted emission compared to the parent  **$\nu$ -DABNA** ( $\lambda_{PL} = 474$  nm, 3 wt% doped in mCBP). Their bluest emitter, **BOBO-Z**, emits at 445 nm, with the same FWHM of 18 nm. Both  $\Delta E_{ST}$  and the delayed lifetime ( $\tau_d$ ) increased to 0.102 eV, and 7.7  $\mu$ s, respectively. The device with this emitter showed pure blue EL ( $\lambda_{EL} = 445$  nm, FWHM = 18 nm,  $E_{QE_{max}} = 13.6\%$ ,  $CIE_y = 0.04$ ). Recently Hatakeyama *et al.* reported a  $\pi$ -extended B,N-doped helicene,  **$\nu$ -DABNA-Mes** that showed efficient and narrowband PL at  $\lambda_{PL} = 484$  nm, FWHM = 16 nm ( $\Delta E_{ST} = 8.5$  meV,  $\tau_D = 2.4$   $\mu$ s,  $\Phi_{PL} = 80\%$ , 1 wt% doped in PMMA).<sup>18</sup> The OLEDs emitted at  $\lambda_{EL} = 480$  nm (FWHM = 27 nm;  $CIE_y = 0.21$ ) and showed an  $E_{QE_{max}} = 22.9\%$ . However, the emission was red-shifted to the sky-blue region due to its extended  $\pi$ -conjugation. We recently reported a B,N-doped heptacene,  **$\alpha$ -3BNMes**, that shows narrowband blue

emission ( $\lambda_{\text{PL}} = 442 \text{ nm}$ , FWHM = 30 nm) in THF.<sup>19</sup> The hyperfluorescent (HF)<sup>20</sup> device with  $\alpha$ -**3BNMes** as a terminal emitter sustained blue EL ( $\lambda_{\text{EL}} = 443 \text{ nm}$ , CIE<sub>y</sub> = 0.1) with an EQE<sub>max</sub> of 15%. Recently, Duan *et al.* reported a B,N-doped pentacene emitter, **mDBIC**, that emits in the deep blue ( $\lambda_{\text{PL}} = 426 \text{ nm}$ , FWHM = 26 nm) region in 2 wt% doped mCP film and was used as the terminal emitter in a HF device that showed excellent performance at the deep blue color point ( $\lambda_{\text{EL}} = 431 \text{ nm}$ , FWHM = 42 nm, EQE<sub>max</sub> = 13.5%, CIE<sub>y</sub> = 0.05).<sup>21</sup> Pushing the emission further into the deep blue in MR-TADF compounds remains exceedingly difficult. The B,N-doped heptacene system  $\alpha$ -**3BNOH** ( $\lambda_{\text{PL}} = 390 \text{ nm}$ ,  $\Delta E_{\text{ST}} = 0.30 \text{ eV}$ ,  $\tau_{\text{d}} = 0.45 \mu\text{s}$ , THF)<sup>22</sup> that we previously reported represents a rare example of a MR-TADF purple emitter as does the B,O-doped triangulene emitter, **DOBNA** ( $\lambda_{\text{PL}} = 398 \text{ nm}$ ,  $\Delta E_{\text{ST}} = 0.18 \text{ eV}$ ,  $\tau_{\text{d}} = 66 \mu\text{s}$ , 1wt% in PMMA).<sup>23</sup>

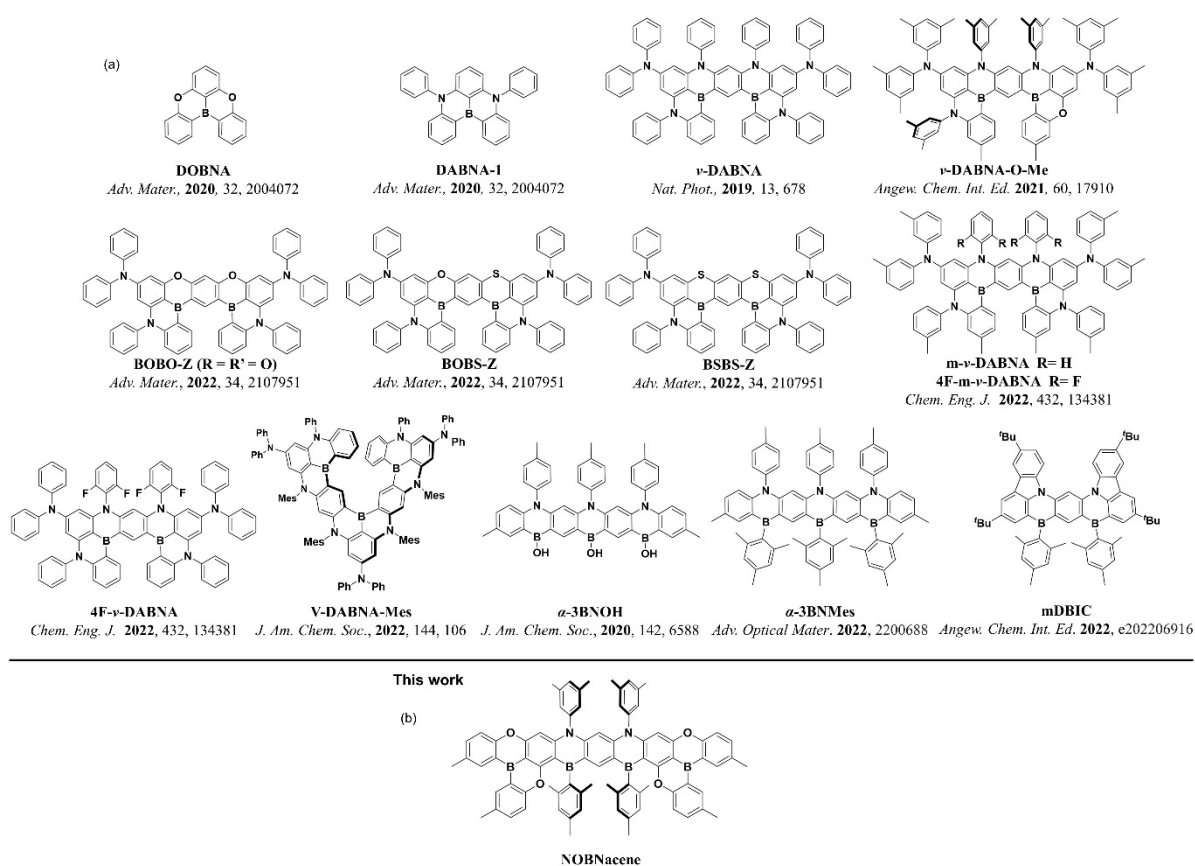


Figure 1. Chemical structures of (a) **DOBNA**, **DABNA-1** and reported  $\pi$ -extended blue MR-TADF emitters. (b) **NOBNacene**.

Building on our recent efforts to design linearly extended MR-TADF acene emitters, here we report a boron-, nitrogen-, and oxygen-doped polycyclic aromatic hydrocarbon that contains nine annulated six-membered rings, **NOBNacene**, (Figure 1b). Despite the apparent large conjugation length, maintaining a regioregularity of the heteroatoms, and using oxygen donors rather than more electron-donating nitrogen atoms results in a deep blue emission in this system. This compound represents arguably the first example of an MR-TADF emitter possessing both electronically distinct donor (N and O) and acceptor groups (two distinct B atoms).<sup>13, 24</sup> In 1.5 wt% TSPO1 doped films, **NOBNacene** shows narrowband emission with a  $\lambda_{\text{PL}}$  of 410 nm, a FWHM of 38 nm, a high  $\Phi_{\text{PL}}$  of 71%, and a thermally activated delayed fluorescence with a  $\tau_{\text{d}}$  of 1.18 ms. The  $\Delta E_{\text{ST}}$  was measured to be 0.30 eV. The corresponding deep blue OLED shows outstanding performance with a maximum external quantum efficiency ( $\text{EQE}_{\text{max}}$ ) of 8.5% at a peak electroluminescence ( $\lambda_{\text{EL}}$ ) of 409 nm (FWHM of 37 nm), with corresponding to Commission Internationale de l'Éclairage coordinates of (0.173, 0.055), very close to the BT.2020 requirement for the blue pixel of (0.131, 0.046).<sup>25</sup> **NOBNacene** combines the benefits of high efficiency, narrow near-UV emission, and high color purity, representing a promising emitter design approach to high-performance deep blue OLEDs.

## Results and Discussion

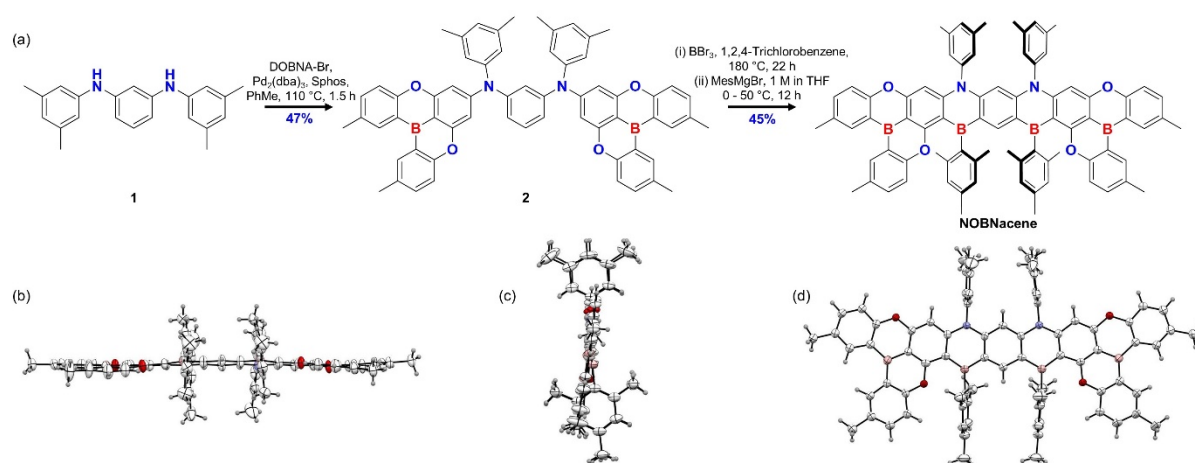


Figure 2. (a) Synthesis of **NOBNacene**. ORTEP diagram of **NOBNacene**, (b), (c) are side views and (d) is a plane view. Thermal ellipsoids show 50% probability.

The convergent synthesis of **NOBNacene** is outlined in Figure 2. Compound **1** was obtained in 68% yield following a Buchwald-Hartwig cross-coupling reaction of 3,5-dimethylaniline with 1,2-dichlorobenzene. The key intermediate **2** was obtained in 47% yield by coupling two equivalents of **DOBNA-Br** with **1**. Electrophilic borylation of **2** with  $\text{BBr}_3$  followed by reaction with excess  $\text{MesMgBr}$  afforded **NOBNacene** in 45% yield. Due to its planar structure, **NOBNacene** is poorly soluble in most common organic solvents. The structure and purity of the emitter were confirmed by  $^1\text{H}$  NMR spectroscopy, high-resolution mass spectrometry (HRMS), high performance liquid chromatography-gel permeation chromatography (HPLC-GPC), and elemental analysis (EA).

Single crystals of **NOBNacene** were obtained by slow evaporation of a saturated solution of the compound in THF over several days at room temperature. The crystal structure is shown in Figures 2b-d. No hydrogen bonding or  $\pi$ - $\pi$  stacking intermolecular interactions were observed for **NOBNacene** in the crystal structure owing to the presence of the highly twisted mesityl and xylyl groups that decorate the nonacene core. As shown in the Figure 2b, the nonacene core of **NOBNacene** remains nearly planar. The B-C<sub>Mes</sub> bond is longer than other bonds in the system, because of this difference in bond lengths the nonacene skeleton is slightly bent as shown in Figure 2d.

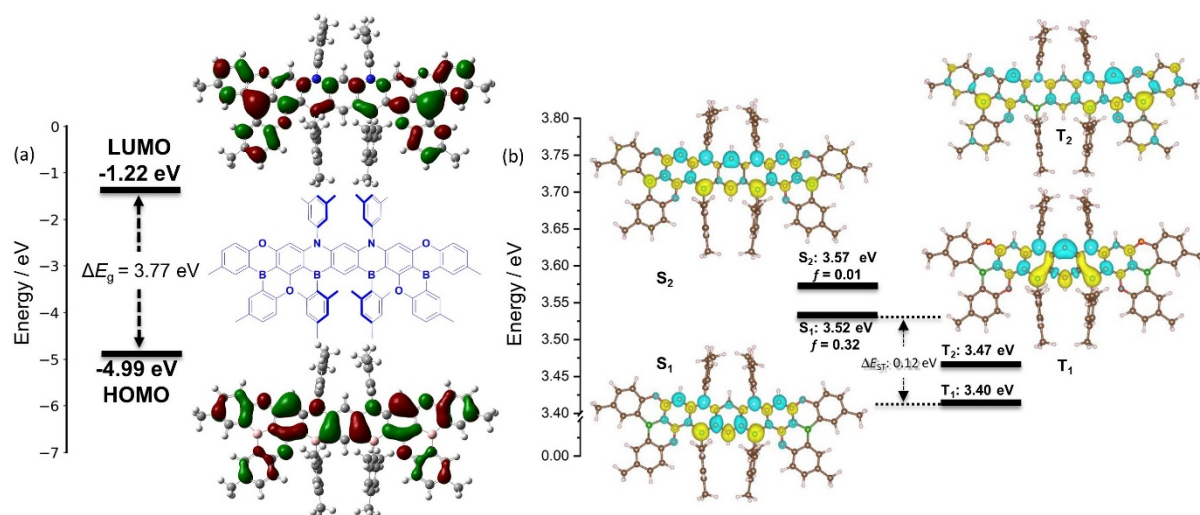


Figure 3. a) HOMO and LUMO electron density distribution and orbital energies of **NOBNacene** calculated at PBE0/6-31G(d,p) in the gas phase (isovalue = 0.02); b) Difference density plots and energies for the two lowest-lying singlet and triplet excited states of **NOBNacene** calculated at SCS-CC2/cc-pVDZ in the gas phase (isovalue = 0.001). The blue color represents an area of decreased electron density, and the yellow color represents an increased electron density between the ground and excited states.  $f$  denotes the oscillator strength for the transitions to the excited singlet states.

The ground [excited] state optimizations were carried out using [Time Dependent-] Density Functional Theory [TD-](DFT) with the PBE0 functional<sup>26</sup> and the 6-31G(d,p)<sup>27</sup> basis set [within the Tamm-Dancoff approximation (TDA)] in the gas phase while the excited states excitation energies were modelled with the spin-component scaling second-order approximate coupled-cluster (SCS-CC2) method. The latter wavefunction-based method has been shown to be essential to model accurately the excited states of MR-TADF emitters.<sup>28</sup> In the ground state (Figure 3a), the HOMO is mainly localized on the atoms of the central benzene ring and the **DOBNA** fragments while the LUMO is mainly localized on the **DOBNA** boron atoms with a very small contribution from the mesityl boranes. The calculated HOMO and LUMO values are -4.99 eV and -1.22 eV, respectively, resulting in a predicted HOMO-LUMO gap of 3.77 eV. This gap is smaller than both **DOBNA** itself (3.97 eV)<sup>23</sup> and the structurally related deep blue B,N-doped heptacene derivatives,  **$\alpha$ -3BNOH** (4.20 eV) and  **$\alpha$ -3BNMes** (4.03 eV).<sup>19, 22</sup>

The difference density plots for the first singlet and triplet excited states show the alternating pattern of increasing and decreasing electron density that is characteristic of MR-TADF emitters. The difference density plots reveal that the electron density in both the S<sub>1</sub> and T<sub>1</sub> states is mostly localized on the electron-rich central part of the molecule. However, the difference density patterns of S<sub>1</sub> and T<sub>1</sub>, while being reminiscent of SRCT excited states, are distinct from each other because of the different one-electron transitions contributions (see supporting information, Tables S1 and S2). The electron density is more diffusely distributed across the entire molecular skeleton in the S<sub>2</sub> and T<sub>2</sub> states. A small  $\Delta E_{S_1T_1}$  value of 0.12 eV is noted for **NOBNacene** (Table S1); however, owing to the different S<sub>1</sub> and T<sub>1</sub> difference density patterns, obtained from vertical excitations from the ground state, it is likely that the vertical  $\Delta E_{S_1T_1}$  would not be accurate, as these excited states would exhibit different relaxation energies.<sup>29</sup> We therefore undertook SCS-CC2 calculations at the optimized S<sub>1</sub> and T<sub>1</sub> geometries and observed that the adiabatic  $\Delta E_{S_1T_1}$  increases to 0.18 eV (Figure S11 and Table S2). An intermediate T<sub>2</sub> state is reported between S<sub>1</sub> and T<sub>1</sub>, obtained from vertical excitation from the ground state, which suggests that RISC could occur through a spin-vibronic coupling mechanism. The S<sub>0</sub>-S<sub>1</sub> transition has a high oscillator strength of 0.32 from calculations with vertical excitation from the ground state, which rises to 0.40 at the relaxed S<sub>1</sub> geometry.

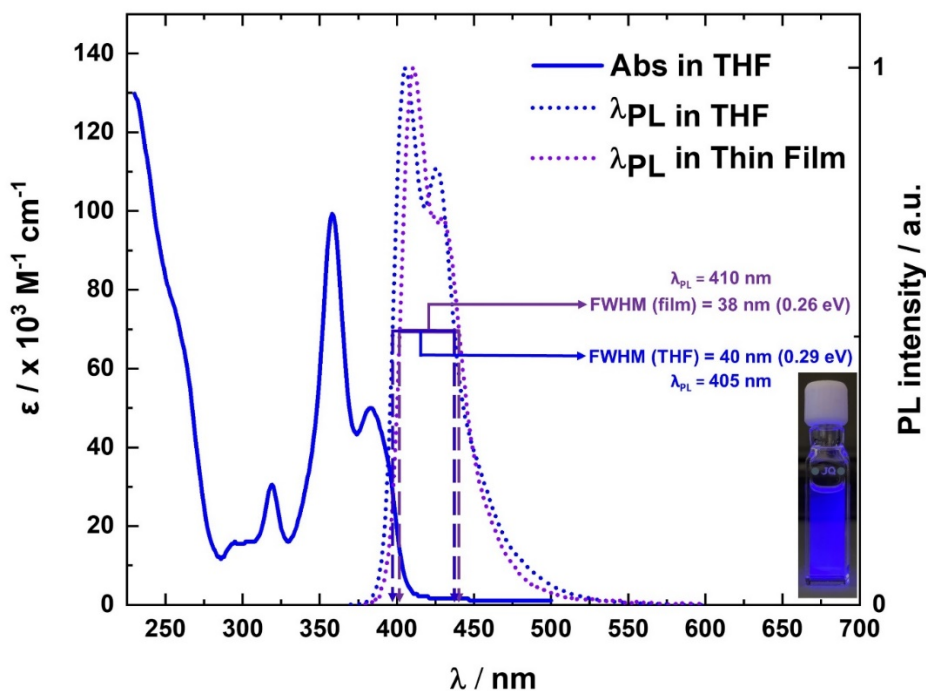


Figure 4. Absorption (blue solid line), steady-state PL in THF at 300 K (blue dotted line), and steady-state PL of the 1.5 wt% evaporated doped thin film in TSPO1 at 300 K (violet dotted line),  $\lambda_{exc.} = 365$  nm. Inset shows the PL of **NOBNacene** in THF at 300 K,  $\lambda_{exc.} = 365$  nm.

### Optoelectronic characterization

We first undertook a photophysical investigation of **NOBNacene** in dilute THF solutions ( $10^{-5}$  M) at 300 K, which would provide insight into understanding the monomolecular properties of this compound. An intense absorption was noted at 229-283 nm with molar absorptivity ( $\epsilon$ ) ranging from  $130$  to  $12 \times 10^3$   $M^{-1} cm^{-1}$ . A well-defined, intense absorption band at 358 nm ( $\epsilon = 99 \times 10^3$   $M^{-1} cm^{-1}$ ) and a lowest energy band at 382 nm ( $\epsilon = 50 \times 10^3$   $M^{-1} cm^{-1}$ ) were observed corresponding to transitions mainly localized on the nonacene core as assigned from the TDA-PBE0/6-31G(d,p) calculations. The absorption profile is similar to that of  **$\alpha$ -3BNOH**<sup>22</sup> and its derivative,  **$\alpha$ -3BNMes**.<sup>19</sup> The lowest energy band in **NOBNacene** is slightly red-shifted compared to that in  **$\alpha$ -3BNOH** ( $\lambda_{abs} = 379$  nm,  $\epsilon = 14 \times 10^3$   $M^{-1} cm^{-1}$ )<sup>22</sup> but significantly blue-shifted from that in  **$\alpha$ -3BNMes** ( $\lambda_{abs} = 419$  nm,  $\epsilon = 18 \times 10^3$   $M^{-1} cm^{-1}$ ). The photoluminescence (PL) of **NOBNacene** in solution is structured and of intermediate broadness (FWHM of 40 nm, 0.29 eV) compared to other reported deep blue MR-TADF emitters, *vide infra*.<sup>10</sup> The emission maximum,  $\lambda_{PL}$ , is at 405 nm and there is a low-energy shoulder at 427 nm. We simulated



the vibronically-resolved emission spectrum within the undistorted harmonic model considering vibrational modes computed at the PBE0/6-31G(d,p) level for the **NOBNacene** model derivative without the mesityl and xylyl substituents. We found that the broadening of the emission is essentially due to three vibrational modes with energies of 178, 643 and 1674  $\text{cm}^{-1}$ . The two lower-frequency modes contribute to the main emission vibronic peak while the highest one leads to the side band (see Figures S13). The  $\Delta E_{\text{ST}}$ , calculated from the difference in the energy of the onsets of the prompt fluorescence and phosphorescence spectra at 77 K in 2-MeTHF, is 0.31 eV (Figure S14a). This value is comparable to those of  **$\alpha$ -3BNOH** ( $\Delta E_{\text{ST}} = 0.25$  eV, 1 wt% in PMMA)<sup>22</sup> and  **$\alpha$ -3BNMes** ( $\Delta E_{\text{ST}} = 0.28$  eV, 1 wt% in PMMA). The photoluminescence quantum yield ( $\Phi_{\text{PL}}$ ) in degassed dilute THF solution is 33%, which decreased under air to 25%. No delayed emission was observed in THF and the lifetime,  $\tau_{\text{PL}}$ , is 22.4 ns (Figure S15).

Table 1. Photophysical properties of **NOBNacene**.

Compound	Medium	$\lambda_{\text{PL}}^c$ / nm	FWHM <sup>d</sup> / nm	$E_{\text{S}_1}^e$ / eV	$E_{\text{T}_1}^e$ / eV	$\Delta E_{\text{S}_1\text{T}_1}^g$ / eV	$\Phi_{\text{PL}}^h$ / %	$\tau_p^i$ / ns	$\tau_d^i$ / ms	$k_{\text{ISC}}^j$ / $\text{s}^{-1}$	$k_{\text{RISC}}^j$ / $\text{s}^{-1}$	$k_{\text{s}_1}^j$ / $\text{s}^{-1}$	$k_{\text{s}_{\text{nr}}}^k$ / $\text{s}^{-1}$
<b>NOBNacene</b>	Sol. <sup>a</sup>	405, 427	40	3.12 <sup>f</sup>	2.81 <sup>f</sup>	0.31	33 <sup>a</sup>	22.3 4	-	-	-	-	-
	film <sup>b</sup>	410, 430	38	3.12	2.82	0.30	71 <sup>b</sup>	2.9	1.18	$2.61 \times 10^8$	$3.74 \times 10^3$	$7.24 \times 10^7$	$1.18 \times 10^7$

<sup>a</sup>In THF solutions ( $10^{-5}$  M). <sup>b</sup>Measured in evaporated thin films consisting of 1.5 wt% emitter in TSPO1 host under vacuum.  $\lambda_{\text{exc}} = 280$  nm. <sup>c</sup>Steady-state emission maximum at 300 K.  $\lambda_{\text{exc}} = 365$  nm. <sup>d</sup>Full width at half maximum of the emission peak. <sup>e</sup> $S_1$  and  $T_1$  energies were obtained from the onsets of the respective prompt fluorescence (delay: 1 ns; gate time: 100 ns) and phosphorescence spectra (delay: 1 ms; gate time: 9 ms) at 77 K.  $\lambda_{\text{exc}} = 343$  nm. <sup>f</sup>2-MeTHF glass ( $10^{-6}$  M). <sup>g</sup> $\Delta E_{\text{ST}} = E(S_1) - E(T_1)$ . <sup>h</sup>Relative photoluminescence quantum yields ( $\Phi_{\text{PL}}$ ) in solutions were measured by the relative method using quinone sulfate as a standard ( $\Phi_r = 54.6\%$  in 1 N  $\text{H}_2\text{SO}_4$ ).<sup>30</sup> Absolute  $\Phi_{\text{PL}}$  of thin films were measured using an integrating sphere. <sup>i</sup>Prompt and delayed lifetimes obtained by TCSPC and MCS, respectively.  $\lambda_{\text{exc}} = 379$  nm. <sup>j</sup>Intersystem and reverse intersystem crossing rates were calculated using steady-state approximation method as described in literature.<sup>31</sup>

We next explored the potential of this compound as an emitter in an OLED. Of the suitably high triplet energy hosts investigated (TSPO1, DPEPO, PPT, and mCP), the highest  $\Phi_{\text{PL}}$  of 71% was obtained when the emitter is doped in TSPO1 host at 1.5 wt%; the  $\Phi_{\text{PL}}$  of this film reduced to 33% upon exposure to air (see Table S3 for host matrix  $\Phi_{\text{PL}}$  study), suggesting strongly that there are accessible triplet excited states. The PL spectrum of **NOBNacene** is red-shifted by 5 nm in the 1.5 wt% TSPO1 doped film compared to in THF solution (Figure 4a). The FWHM of the emission spectrum in the doped film is 38

nm (0.26 eV). The high-energy peak around 410 nm is the dominant one and there is a low-energy shoulder at 430 nm, consistent with the theoretical calculations. The emission of **NOBNacene** is redshifted by 12 nm from **DOBNA** ( $\lambda_{\text{PL}} = 398$  nm,  $\Phi_{\text{PL}} = 58\%$ , in 1 wt% PMMA).<sup>23</sup> The  $\Delta E_{\text{ST}}$  is 0.30 eV in the 1.5 wt% TSPO1 thin film, a value that is nearly identical to that observed in 2-MeTHF (Figure S14).

Temperature-dependent transient PL analysis was carried out to identify the nature of the triplet harvesting in **NOBNacene**. We observed a biexponential emission decay with associated prompt ( $\tau_{\text{p}}$ ) and delayed ( $\tau_{\text{d}}$ ) lifetimes of 2.90 ns and 1.18 ms, respectively (Figures 5a and 5b). The prompt component shows no temperature dependence, while the intensity of the delayed emission increases above 250 K. The temperature dependence of the delayed emission provides confirmation that **NOBNacene** is TADF active. TADF in emitters with large  $\Delta E_{\text{ST}}$  have previously been reported by Lu *et al.*<sup>32</sup> in a D-A type violet emitter **CZ-MPS** that exhibited a very long  $\tau_{\text{d}}$  of 4.85 ms linked to a  $\Delta E_{\text{ST}}$  of 0.58 eV. The authors ascribed the TADF to proceeding via intermediate triplet states. The  $k_{\text{RISC}}$  value of **NOBNacene** was calculated to be  $3.74 \times 10^3$  s<sup>-1</sup>, which is slower than what reported for **DOBNA** ( $1.6 \times 10^4$  s<sup>-1</sup>, in 1 wt% PMMA)<sup>23</sup>, but faster than for  $\alpha$ -**3BNMes** ( $5.9 \times 10^2$  s<sup>-1</sup>, in 1 wt% PMMA).<sup>19</sup>

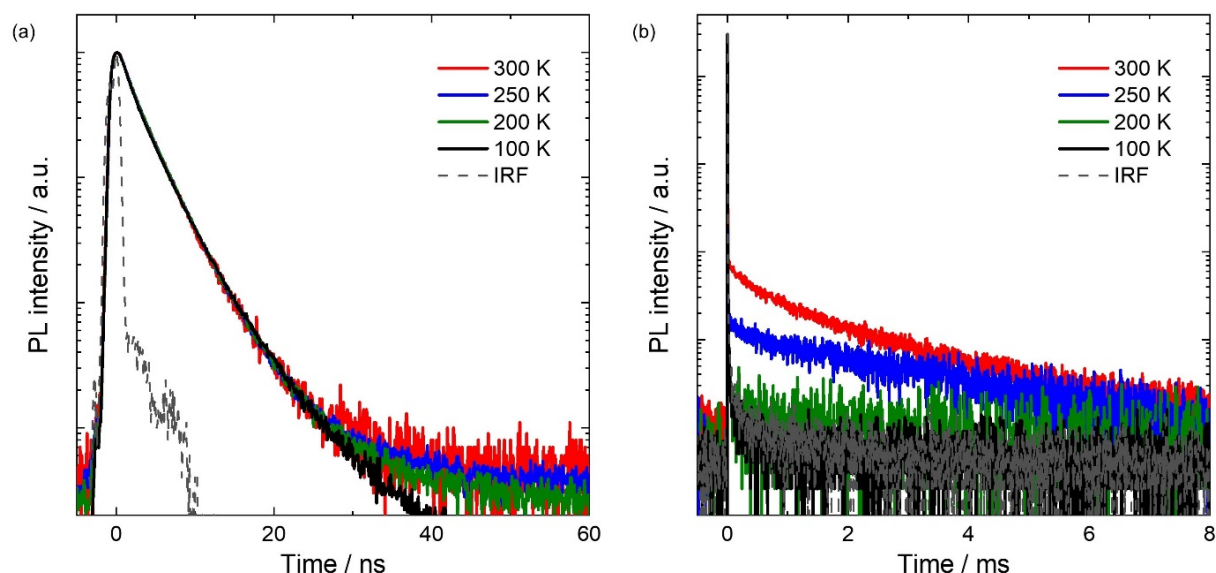


Figure 5 Time-resolved PL decays of **NOBNacene** doped thin films ( $c_{\text{D}} = 1.5$  wt% in TSPO1 host) under various temperatures from 300 K to 100 K. The measurements were performed by using TCSPC with samples loaded in a cryostat in vacuum. (a) TCSPC at a 100 ns time scale, (b) MCS at a 10 ms

time scale. IRF is instrumental response function. The excitation wavelength was 379 nm and the PL emission at 410 nm was recorded.

## **OLEDs**

Given the high-energy emission, the choice of host matrix with suitable high triplet energies is very limited. From the photophysical study TSPO1 was identified as the most suitable host matrix to be used in the OLED. The optimized device structure used was: ITO/ HAT-CN (5 nm)/ NPB (40 nm)/ TCTA (10 nm)/ CzSi (10 nm)/ **NOBNacene** (1.5-6.0 wt%) : TSPO1 (20 nm)/TSPO1 (10 nm)/ TmPyPB (20 nm)/LiF (0.8 nm)/Al (100 nm), where HAT-CN, NPB, TCTA, CzSi, TSPO1, TmPyPB, LiF are the hole injection, hole transporting, electron blocking, exciton blocking, hole blocking, electron transporting, and electron injection layers, respectively. The device structure and energy levels of each layer are illustrated in Figure S17. OLED devices were fabricated using  $c_D$  of 1.5 wt%, 3.0 wt%, and 6.0 wt% to understand its effects on both carrier transport and color purity.

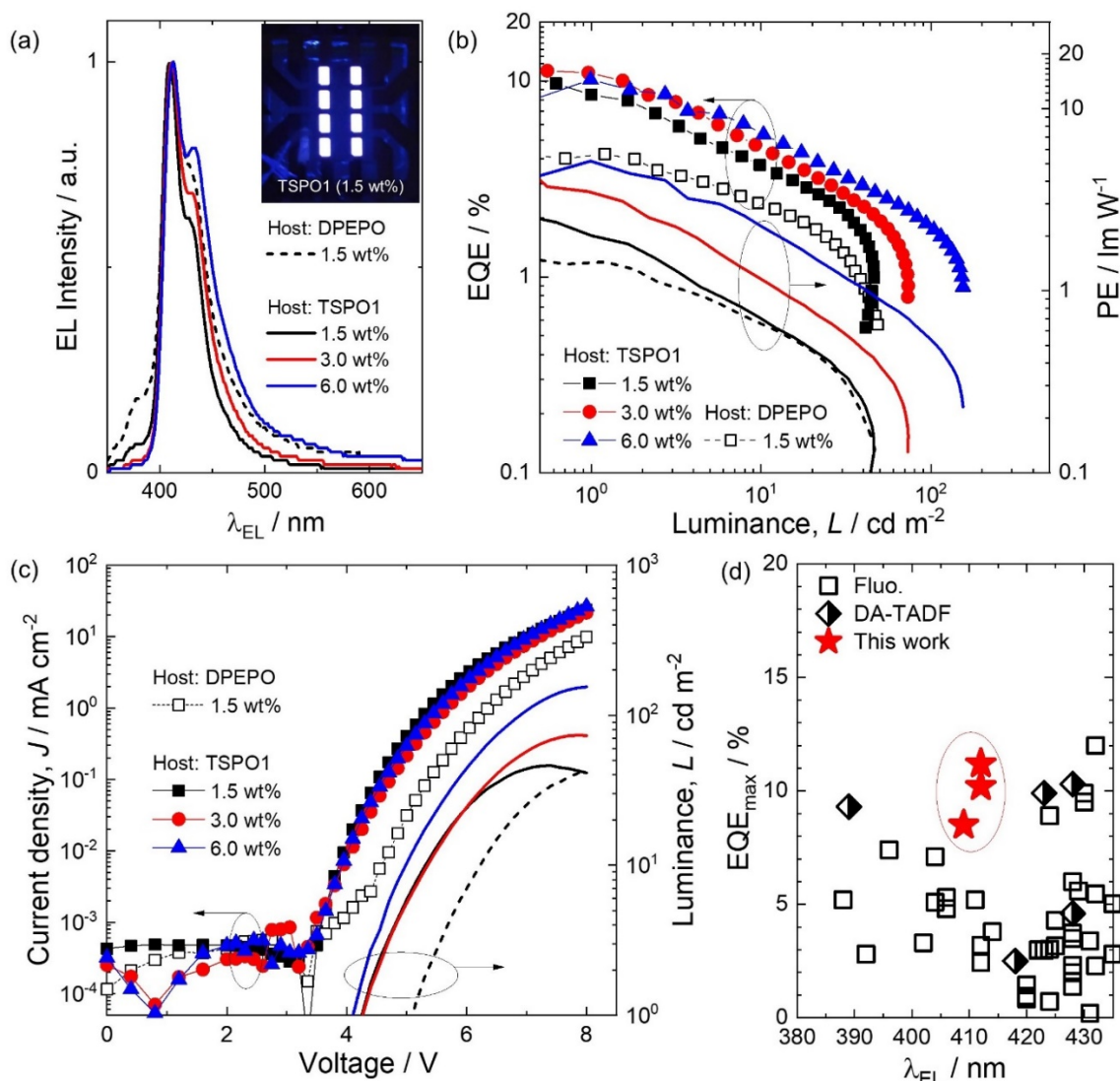


Figure 6. OLED device performance for **NOBNacene** in both DPEPO and TSPO1 host. a) EL spectrum of devices at 6 V. Inset shows Image of an operating TSPO1 device ( $c_D = 1.5$  wt%) under 6 V. b) Dependence of external quantum efficiency (EQE) and power efficiency (PE) on the luminance. c) Current density-voltage-luminance (J-V-L) characteristics of the device. d) EQE<sub>max</sub> comparison in terms of EL peak wavelength to reported fluorescent (Fluo.) and D-A type TADF emitters. source references for the plotted data are given in Table S4 and compared with literature devices.

The device with  $c_D$  of 1.5 wt% in TSPO1 host presented narrow violet emission with a maximum at  $\lambda_{EL}$  of 411 nm (FWHM = 37 nm) and a shoulder at 428 nm, which are assigned as vibronic bands. The EL matches well the PL of the film at the same  $c_D$  ( $\lambda_{PL} = 410$  nm, FWHM = 38 nm, 1.5 wt% in TSPO1). At 3 wt% doping concentration, the  $\lambda_{EL}$  is nearly unchanged at 412 nm compared to the EL of the 1.5 wt% device; however, the FWHM increased slightly to 41 nm and the shoulder at 428 nm is more pronounced. The  $\lambda_{EL}$  of the device with  $c_D$  of 6.0 wt% is essentially the same (412 nm); however, there

is significant broadening of the EL (FWHM = 47 nm) due to the more pronounced shoulder at 428 nm. The broadening of emission for fused planar emitters at a higher concentration is common due to intermolecular interaction in the emitting layers.<sup>33</sup> Due to its high  $E_T$ , we also fabricated devices using DPEPO as the host at the same  $c_D$  of 1.5 wt% for comparison purposes. Besides the lower EQE, the EL spectrum is broadened (FWHM = 44 nm) and the turn-on voltage is higher by 0.9 V in the DPEPO device compared to that in TSPO1. In addition, the device showed incomplete electron confinement within the EML as evidenced by the high-energy EL peak at 380 nm, which was assigned to emission from the TCTA layer.

The CIE coordinates of the TSPO1 devices with  $c_D$  of 1.5 wt% are (0.173, 0.055), values that are very close to the Rec.2020 standard for primary blue in UHDTV (0.131, 0.046).<sup>25</sup> Increasing the doping concentration of the emitter resulted in the expected reduced colour purity of the device, reflected in the CIE coordinates of (0.176, 0.068) and (0.187, 0.103), respectively, for the 3 wt% and 6 wt% devices. The  $EQE_{max}$  ( $PE_{max}$ ) were 8.5% ( $2.06 \text{ lm W}^{-1}$ ), 11.2% ( $3.51 \text{ lm W}^{-1}$ ) and 10.2% ( $5.19 \text{ lm W}^{-1}$ ) for devices with  $c_D$  of 1.5 wt%, 3.0 wt% to 6.0 wt%, respectively. The high EQE (11.2%) of the device at this deep blue chromaticity ( $CIE_y < 0.08$ ) is among the highest recorded to date (Figure 6d). The device data are summarized in Table S4. A linear dependence of luminescence to current density (Figure S18) and the presence of delayed component in the transient PL analysis provide strong indications that triplet harvesting in the device occurs through TADF. Despite the high  $EQE_{max}$ , the efficiency roll-off in each system is severe, which is likely due in part to the large  $\Delta E_{ST}$  of the emitter,<sup>33</sup> the long delayed lifetimes that result in increased TTA and STA processes, and the instability of the phosphine oxide-based host<sup>34</sup>.

Table 2. Device data of **NOBNacene** in TSPO1 and DPEPO host.

Host	$c_D$ / wt%	$V_{on}$ / V	$\lambda_{EL}$ / nm	FWHM / nm	CIE (x,y)	$EQE_{max}$ / %
TSPO1	1.5	4.2	409	37	(0.173, 0.055)	8.5
	3.0	4.2	412	41	(0.176, 0.068)	11.2
	6.0	4.1	412	47	(0.187, 0.103)	10.2
DPEPO	1.5	5.1	411	44	(0.196, 0.106)	4.2

## Conclusions

Herein, we demonstrate an easy-to-access synthetic route to construct a boron, nitrogen, and oxygen doped ladder type nonacene. The emitter **NOBNacene** is the first example of a  $\pi$ -extended MR-TADF emitter that has nine, six-membered rings fused along one dimension. Strikingly, this  $\pi$ -extended design shows only a limited conjugation length, reflected in emission in the deep blue region in THF solution ( $\lambda_{\text{PL}} = 405$  nm, FWHM = 40 nm,  $\Phi_{\text{PL}} = 33\%$ ) and in the 1.5 wt% TSPO1 film ( $\lambda_{\text{PL}} = 410$  nm, FWHM = 38 nm,  $\Phi_{\text{PL}} = 71\%$ ,  $\tau_{\text{d}} = 1.77$  ms). This emitter design utilizes two electronically distinct boron acceptor atoms and a combination of nitrogen and oxygen donor atoms. Deep blue EL ( $\lambda_{\text{EL}} = 409$  nm, FWHM = 37 nm) was produced when **NOBNacene** was employed as the emitter in the OLED. An  $\text{EQE}_{\text{max}}$  of 8.5% at CIE coordinates of (0.173, 0.055) was achieved. The  $\text{EQE}_{\text{max}}$  could be enhanced to 11.3% at a higher emitter doping of 3 wt%, with only a small loss in the color purity, reflected in CIE coordinates of (0.176, 0.068). The  $\text{EQE}_{\text{max}}$  values reported here are among the highest reported for deep-blue OLED devices where the  $\lambda_{\text{EL}} < 420$  nm.

## Supporting Information

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, GCMS, HRMS and reverse phase and gel permeation (GPC) HPLC; supplementary computational data and coordinates; Crystallographic data (CIF). **NOBNacene** (CCDC 2212087). Additional photophysical and OLED data.

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## TOC

