Boron-Based Narrowband Multiresonance Delayed Fluorescent Emitters for Organic Light-Emitting Diodes

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Dedicated to Prof. Jun Yeob Lee (Sungkyunkwan University, Korea) and Prof. K. R. Justin Thomas (IIT Roorkee, India) on occasion of their 52nd and 55th birthdays, respectively.

Recently, the exploration of boron (B)/heteroatom-embedded polycyclic nanographites featuring multiresonance thermally activated delayed fluorescence (MR-TADF) garners astonishing attention to promote the advancement of organic light-emitting diodes (OLEDs). Contrary to the traditional donor–acceptor (D–A)-type TADF emitters, the MR-TADF emitters manifest narrowband emission with full width at half maximum (FWHM ≤ 40 nm) and superior photoluminescence quantum yield (PLQY) coupled with the small singlet–triplet energy splitting, which appeal their potential as promising candidates in fabricating efficient OLEDs. Growingly, MR-TADF emitters deliver benchmark device performance comparable to the conventional TADF/phosphorescent emitters. However, they are suffering from the major drawbacks such as difficult to realize full-color emitters, slow exciton upconversion dynamics, aggregation-caused emission quenching, severe efficiency roll-off, and poor operational lifetime, which jeopardizes their practical applicability. Herein, a comprehensive review on B-based MR-TADF emitters reported till date is presented, focusing on the different design strategies documented for circumventing the aforementioned shortcomings. This review is divided into several subgroups based on the emission color of the materials to draw the attention of organic electronics community toward constructing efficient full-color MR-OLEDs. Finally, challenges and opportunities in the MR-TADF emitters are discussed.

1. Introduction

Since their first demonstration, organic light-emitting diodes (OLEDs) gained tremendous impetus because of their unprecedented advantages over the traditional liquid crystal displays (LCDs) such as lightweight, color tunability, low power consumption, inexpensive, wide viewing angles, color purity, and fast response time.[1–11] Particularly, the capacity to fabricate OLEDs on flexible/rollable substrates appeals to their potential application in future display and solid-state lightings.[12–18] Growingly, OLEDs have penetrated into the commercial market and now widely using in the consumer electronics such as mobile phone displays, digital cameras, vehicle displays, and ultrahigh-definition televisions (UHDTV).[19–23] The OLED performance is mainly governed by the organic emitters and device engineering. Indeed, organic emitters play an essential role in controlling the color purity, operational lifetime, efficiency, and overall device performance.[26–28] Therefore, the development of efficient organic emitters for OLEDs is indispensable. Generally, the recombination of injected charge carriers in OLED forms a 1:3 ratio of singlet and triplet excitons.[29–33] Spin selection rule allows conventional organic emitters to utilize only singlet excitons for light emission, which limits their internal (IQE) and external quantum efficiencies (EQEs) to 25% and 5%, respectively.[33–35] To circumvent this, over the last few decades there has been an expeditious upsurge in developing triplet exciton harvesting emitters. In the initial attempts, noble metal (Ir and Pt) containing inorganic complexes were used as emitters due to their ability to exploit triplet excitons via the phosphorescence mechanism.[35,36] However, the toxicity and cost-effective of noble metals truncate their practical applicability. To this end, efforts have been devoted to the development of pure organic emitters which can exploit triplet excitons for light emission through delayed fluorescence. In this regard, thermally activated delayed fluorescence (TADF) emerged as a promising strategy because it can effectively transform the triplet excitons into a singlet state via reverse intersystem crossing (RISC) by mitigating...
the energy gap ($\Delta E_{\text{ST}}$) between the lowest singlet ($S_1$) and triplet excited ($T_1$) states with the aid of judicious molecular design (Figure 1).[30–39] Conventional TADF emitters are generally constructed by the donor–acceptor (D–A) configuration for effective separation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which is crucial for achieving low $\Delta E_{\text{ST}}$ and accelerating RISC.[40–49] Although the device performance of the state-of-the-art D–A-type TADF emitters reached the level of the conventional phosphorescent emitters, their unavoidable intrinsic intramolecular charge transfer (ICT) characteristic inevitably leads to the broad emission with large full width at half maximum ($\text{FWHM} \geq 70 \text{ nm}$).[50,51] Such broad emission negatively impacts the color purity of the emitters and imperils their practical applicability, which needs to be resolved from the molecular design perspective.[52–63]

In 2016, Hatakeyama et al. proposed a unique molecular design called multiple-resonance-induced TADF (MR-TADF), in which the electron-deficient boron (B) and electron-rich heteroatom (N/O) embedded in a fused polycyclic nanographene system.[62,63] The complementary resonance effects of heteroatom and B substantially enable atomically separated HOMO and LUMO orbitals on their adjoining ortho- and para-carbon atoms, respectively, endowing them with low $\Delta E_{\text{ST}}$, which turn on the TADF emission.[62–64] The most intriguing advantage of these so-called MR-TADF emitters is their narrow emission with FWHM $< 40 \text{ nm}$, which is enabled by the suppressed vibronic coupling and structural alterations in the excited state (Figure 2).[62,63] These combining merits of high exciton utilization efficiency and narrow FWHM render them ideal emitters for OLEDs with high electroluminescence efficiency and unprecedented color purity comparable to the quantum dots and perovskites.[64–82] Consequently, MR-TADF emitters fascinated the researchers and the burgeoning number of MR molecules have been documented during the last 7 years. Although MR-TADF emitters delivered benchmark device performance with EQE $\geq 35\%$, they suffer from few major obstacles: 1) The fused molecular skeleton on which atomically separated HOMO and LUMO orbitals induce only limited ICT character, which makes them difficult to realize bathochromic-shifted emission from a blue region with the prerequisite of narrow FWHM. However, fabrication of full color OLED requires not only blue emitters, but also ultrapure green and red emitters.[83–85] 2) Although the conceptual advancement has been derived numerous MR-TADF emitters, unlike conventional TADF emitters, they often possess low spin-up conversion rates ($k_{\text{RISC}} \approx 10^4 s^{-1}$), which leads to the severe efficiency roll-off at practical brightness. 3) Their inherited planar molecular confirmation often prone to detrimental aggregation-caused emission quenching. 4) The MR-TADF emitters demonstrated poor operational stability, which is critical parameter for practical applications. Followed
by the seminal report, tremendous efforts have been devoted to overcome the aforementioned shortcomings of MR-TADF emitters.[21,64–82] However, to the best of our knowledge no detailed review has been reported focusing on the different design strategies reported for mitigating the abovementioned obstacles of MR-TADF emitters. To fill this gap, herein we present a comprehensive review highlighting on the recent advances in the molecular designs of B-based MR-TADF materials to produce wide-color gamut emitters with concurrently achieving high $k_{\text{RISC}}$, low efficiency roll-off, and long operational stability.

Initially, Hatakeyama et al. unveiled the first examples of a series of wide bandgap MR-featured B- and O-embedded PAHs (Figure 3).[61] Among them, 2a and its derivatives were used as an MR-type acceptor for constructing D–A TADF emitters by tethering it with various donor units.[80–93] Albeit they demonstrated excellent EQEs > 30%, often they exhibit broad emission with FWHM > 50 nm and poor color purity (Figure 3). Thus, efforts have been devoted to the development of MR core, which can exhibit efficient TADF property together with narrow emission and uncompromised EQE.

### 2. Blue/Deep-Blue MR-TADF Emitters

To this end, in 2016, Hatakeyama et al. reported an enticing design strategy by replacing the oxygen in 2a with tricoordinate N-atom, resulted in B/N-containing MR-TADF chromophores (Chart 1). The opposite resonance effect of N- and B-atoms enabled atomically separated HOMO and LUMO orbitals, which endowed them with a low $\Delta E_{\text{ST}}$. Initially, they reported two new blue MR-TADF emitters named DABNA-1 and DABNA-2.[62]

The compounds showed redshifted emission compared to the B,O-MR cores ascribed to the strong Lewis basic character of N-atom compared to O-atom. Indeed, DABNA-2 exhibited much redshifted emission than DABNA-1 because of the auxochromic effect of phenyl and diphenylamine substituents. Most importantly, unlike the conventional TADF emitters, these N/B-containing MR-TADF chromophores revealed very narrow FWHM ≈ 33 nm. The photophysical analysis revealed low $\Delta E_{\text{ST}}$ of 0.18 and 0.15 eV for DABNA-1 and DABNA-2, respectively (Table 1), which is sufficient to trigger the TADF emission (Table 3). Consequently, the compounds DABNA-1 and DABNA-2 showed short $\tau_d$ and decent $k_{\text{RISC}}$ of 93.7 μs/$9.3 \times 10^3$ s$^{-1}$ and 65.3/$14.8 \times 10^3$ s$^{-1}$, respectively. Further, the applicability of these emitters in OLED was evaluated in the mCBP host, and DABNA-1 showed deep-blue emission with $\lambda_{\text{EL}}$ of 459 nm and FWHM of 28 nm, CIE(x,y) of (0.13, 0.09) (Table 2). The EQE$^{\text{max}}$/CE of the DABNA-1-based device is 13.5%/10.6 cd A$^{-1}$. However, DABNA-2-based device demonstrated impressive performance with EQE$^{\text{max}}$ of 20.2%/CE of 21.1 cd A$^{-1}$, indicating its 100% IQE. Although DABNA-2 showed redshifted emission, its FWHM ≈ 28 nm is as good as DABNA-1. These results indicate that N/B-containing MR-TADF emitters could be a promising candidate for fabricating efficient OLEDs with excellent color purity.

Later, Lee et al. developed tert-butyl-modified DABNA-1, named t-DABNA, to suppress the aggregation-caused emission quenching by reducing the intermolecular interactions with the help of tert-butyl units.[78] The t-DABNA showed a 5 nm redshifted emission and slightly reduced $\Delta E_{\text{ST}}$, 0.17 eV compared to DABNA-1, but it displayed a long $\tau_d$ of 93.7 μs, like DABNA-1 (83.3 μs). Initially, they tested these materials as dopants in the DPEPO host and showed EQE$^{\text{max}}$ of 25% and 18.7% for t-DABNA and DABNA-1, respectively. The superior performance of t-DABNA was attributed to its high PLQY, and suppressed aggregation-caused emission quenching. Nonetheless, both the emitters showed severe efficiency roll-off at practical brightness because of their long $\tau_d$. To overcome this, they used DMAC-DPS as an assistant dopant to reduce the triplet exciton accumulation. The DMAC-DPS possesses a very short $\tau_d$ ≈ 5.6 μs and high $k_{\text{RISC}}$ of $2.53 \times 10^3$ s$^{-1}$. The device with DPEPO:30% DMAC-DPS:1% t-DABNA or DABNA-1 demonstrated EQE$^{\text{max}}$ of 31.4% and 23.5% at 1 cd m$^{-2}$ for t-DABNA and DABNA-1, respectively, and even it maintained high EQE of 19.8% and 15.6% at 1000 cd m$^{-2}$. The improved performance of these devices compared to the former device containing DPEPO host was ascribed to the reduced triplet excitation concentration in MR-TADF emitters; this was also confirmed by the TRPL analysis of the doped films with and without assistant dopant. The assistant dopant-featured t-DABNA device showed a short $\tau_d$ of 6.3 μs compared to the DPEPO hosted device of 83.3 μs. The authors also presented the operational lifetime of t-DABNA with and without an assistant dopant. Although the assistant dopant-based device displayed 10 times longer lifetime than DPEPO hosted device, it showed a short device lifetime of 30 h ($LT_{50}$) at 100 cd m$^{-2}$ may be due to the poor stability of the host and assistant dopant. Further, to improve the lifetime of DABNA-based MR-TADF cores, the same group was used t-DABNA and DABNA-1 as fluorescent dopants rather than TADF dopants to avoid triplet exciton quenching. They used anthracene-based ADN as a wide bandgap host due to its low $\Delta E_{\text{ST}}$. Initially, they reported two new blue MR-TADF emitters, viz., B-O-dpa, B-O-Cz, B-O-dmAc, and B-O-dpAc, respectively.[110] The design is based on replacing the one electron-rich N-atom with a relatively low electron-rich O-atom to shift the emission of the compounds into blue region.

![Figure 3. Design of MR-core featured D–A type TADF emitters.](Image)
Besides, the aromatic units such as diphenylamine, carbazole DMAc, and diphenyl acridine donors benefited to manage the light emission properties. In the series, the B-O-dpa displayed pure-blue emission, $\lambda_{PL} \approx 443$ nm, FWHM $\approx 28$ nm. The acridine-substituted derivatives showed accelerated $k_{RISC}$ attributed to the improved ICT character. Further, the TADF...
Table 1. Physicochemical properties of deep-blue/blue MR-TADF emitters.

| Dye          | λ<sub>em</sub> [nm], (sol/film) | FWHM (sol/film) | Φ<sub>v</sub> (sol/film), [%] | S<sub>v</sub>/T<sub>v</sub>/ΔE<sub>CT</sub> [eV] | τ<sub>v</sub> [ns]/τ<sub>i</sub> [μs] | T<sub>On</sub> [°C] | References |
|--------------|---------------------------------|-----------------|-----------------------------|-----------------------------------|-----------------------------|---------------|------------|
| DABNA-1      | 462/464                         | 33/30           | 89/88                       | 2.67/2.49/0.18                    | 9.5/--          | --           | [62]       |
| DABNA-2      | 470/475                         | 34/40           | 85/90                       | 2.61/2.47/0.14                    | 6.0/--          | --           |           |
| t-DABNA      | --                              | --              | --                          | 2.80/2.63/0.17                    | --/83.3         | 418          | [73]       |
| s-DABNA      | 468/467                         | 14/18           | 74/90                       | 2.66/2.62/0.017                   | 41/4.3          | --           | [94]       |
| PAB          | 449/453                         | --/23           | --60                        | 2.77/2.71/0.05                    | 7.9/55.7        | 372          | [69]       |
| 2IPAB        | 456/457                         | --/26           | --67                        | 2.76/2.68/0.1                     | 8.1/76.6        | 392          |           |
| 3IPAB        | 456/458                         | --/23           | --75                        | 2.78/2.68/0.1                     | 7.2/74.2        | 374          |           |
| B2           | --/455                          | --/32           | --53                        | 2.73/2.55/0.18                    | --              | --           | [95]       |
| B3           | --/441                          | --/34           | --33                        | 2.88/2.66/0.22                    | --              | --           |           |
| B4           | --/450                          | --/38           | --57                        | 2.76/2.61/0.15                    | --              | --           |           |
| s-DABNA-Mes  | --/484                          | --/16           | --80                        | 2.56/2.60/0.05                    | 6.9/2.39        | --           | [96]       |
| s-DABNA-O-Me | --/464                          | --/24           | --90                        | 2.67/2.75/0.029                   | 5.1/7.7         | --           | [67]       |
| BOBO-Z       | 441/445                         | 15/18           | 76/64                       | --/0.10                           | 2.3/7.7         | --           | [97]       |
| BOBS-Z       | 453/457                         | 21/24           | 94/93                       | --/0.12                           | 1.1/7.6         | --           |           |
| BSBS-Z       | 460/464                         | 20/22           | 93/88                       | --/0.12                           | 1.0/6.7         | --           |           |
| m-s-DABNA    | 464/--                          | 14/--           | --90.5                      | 2.81/2.84/0.07                    | 8.4/3.09        | --           | [98]       |
| 4F-s-DABNA   | 457/--                          | 14/--           | --90.2                      | 2.84/2.79/0.05                    | 8.7/3.12        | --           |           |
| 4F-m-s-DABNA | 455/14                         | 88.5            | 2.86/2.79/0.07              | 8.2/0.19                         | --              |           |
| 3BNOH        | 390/395                         | 31/32           | 50/--                       | --/0.31                           | 0.4/55          | 554          | [99]       |
| mBP-DABNA-Me | 464/467                         | 28/--           | 97/--                       | --/0.12                           | 7.6/64          | --           | [100]      |
| BSBS-N1      | 473/478                         | 21/24           | 59/89                       | 2.59/2.45/0.14                    | 0.9/5.6         | 377          | [101]      |
| B-O-dpa      | 433/--                          | 28/--           | --86                        | 2.95/2.77/0.18                    | 10/224          | --           | [102]      |
| B-O-Cz       | 441/27                         | --/--           | --94                        | 2.87/2.72/0.15                    | 16/51           | --           |           |
| B-O-dmAc     | 461/38                         | --/--           | --91                        | 2.77/2.66/0.11                    | 9/123           | 100          |           |
| B-O-dpAc     | 463/38                         | --/--           | --94                        | 2.76/2.70/0.06                    | 8/83            | 143          |           |
| CBN0         | 443/450                         | 23/30           | --96                        | 2.97/2.76/0.21                    | 7/148           | --           | [103]      |
| DMAcBN0      | 462/470                         | 34/41           | --99                        | 2.89/2.66/0.23                    | 7.3/129         | --           |           |
| DPacBN0      | 462/468                         | 33/39           | --98                        | 2.86/2.67/0.19                    | 7.5/100         | --           |           |
| tCBNDADPO    | 466/470                         | 26/47           | --99                        | 3.00/2.55/0.45                    | 2.6/1.9         | 444          | [104]      |
| tDABNA-dtB   | 465/22                         | 22/--           | 97/--                       | 2.77/2.58/0.19                    | 7.1/109         | 441          | [105]      |
| SF1-BN       | 493/23                         | 23/93           | 2.52/2.39/0.13              | 16.3/9.45                        | 460             | [106]       |
| SF3-BN       | 493/25                         | 90/--           | 2.55/2.40/0.15              | 16.8/260                         | 497             |           |
| BN1          | 454/18                         | 18/--           | --91                        | 2.83/2.63/0.20                    | 4.3/126.6       | 443          | [95]       |
| BN2          | 464/15                         | 15/--           | --93                        | 2.75/2.59/0.16                    | 3.4/74.6        | 448          |           |
| BN3          | 456/17                         | 17/--           | --98                        | 2.79/2.64/0.15                    | 1.3/17.8        | 478          |           |
| DPACcBN1     | 469/479                         | 23/31           | 98/--                       | 2.65/2.54/0.11                    | 4.9/116         | 326          | [107]      |
| DPACcBN2     | 460/470                         | 22/29           | 92/--                       | 2.71/2.59/0.12                    | 4.1/54          | 411          |           |
| DPACcBN3     | 468/475                         | 20/27           | 94/--                       | 2.67/2.54/0.13                    | 2.6/69          | 442          |           |
| PTZBN1       | 490/41                         | 41/88           | 2.67/2.51/0.16              | 4.8/33.5                         | --              | [108]       |
| PTZBN2       | 483/41                         | 41/95           | 2.71/2.56/0.15              | 4.5/22.4                         | --              |           |
| PTZBN3       | 468/30                         | 98/--           | 2.79/2.62/0.17              | 5.8/26.5                         | --              |           |
| CBO          | 445/448                         | 26/29           | 98/99                       | --/0.16                           | 6.7/120         | --           | [109]      |
| CbS          | 471/472                         | 28/30           | 99/98                       | --/0.14                           | 4.6/30          | --           |           |
| CbSe         | 477/479                         | 33/34           | 98/98                       | --/0.15                           | 0.8/14          | --           |           |
| Compound        | Device structure          | EQE<sub>(max)/1000 cd/m<sup>2</sup> | CE, cd/A | PE, lm/W | λ<sub>EL</sub>/FWHM [nm] | CIE<sub>(x,y)</sub> | References |
|-----------------|---------------------------|-----------------------------------|--------|--------|------------------------|-------------------|------------|
| DABNA-1         | ITO/NPD/TCTA/mCP/EM/LTSPO<sub>1</sub>/LiF/Al | 13.5/– | 10.6 | 8.3 | 459/28 | 0.13, 0.09 | [62] |
| DABNA-2         | ”                          | 20.2/– | 21.1 | 15.1 | 467/23 | 0.12, 0.13 | ” |
| tDABNA          | ITO/PEDOT:PSS/TAPc/mCP/EM/LTSPO<sub>1</sub>/TPBi/LiF | 31.4/19.8 | 32.1 | 33.3 | – | – | [73] |
| s-DABNA         | ITO/NPD/TCTA/mCP/EM/LTSPO<sub>1</sub>/LiF/Al | 34.4/26.0 | 31.0 | – | 469/18 | 0.12, 0.11 | [94] |
| PAB             | ITO/MoO<sub>3</sub>/TAPc/mCP/EM/DPEPO/TmPyPB/LiF/Al | 14.7/– | 10.4 | 7.1 | 456/31 | 0.14, 0.07 | [69] |
| 2iPAB           | ”                          | 16.8/– | 11.8 | 8.0 | 456/27 | 0.14, 0.07 | ” |
| 3iPAB           | ”                          | 19.3/– | 34.4 | 10.2 | 460/27 | 0.14, 0.07 | ” |
| B2              | ITO/NPD/TCTA/mCP/EM/LTSPO<sub>1</sub>/LiF/Al | 18.3/– | 16.7 | 13.8 | 460/37 | 0.13, 0.11 | [95] |
| s-DABNA-Mes     | ITO/NPD/TCTA/mCP/EM/LTSPO<sub>1</sub>/LiF/Al | 22.9/10.9 | 26.7 | – | 480/27 | 0.09, 0.21 | [96] |
| BOBO-Z          | ITO/HATCN/TAPc/mMCPEML/PFP/B3PyPB/LiF/Al | 13.6/3.3 | 7.2 | 5.0 | 445/18 | 0.15, 0.04 | [97] |
| BOBS-Z          | ”                          | 26.9/15.0 | 16.7 | 12.9 | 456/23 | 0.14, 0.06 | ” |
| BSBS-Z          | ”                          | 26.8/15.9 | 23.2 | 15.0 | 463/22 | 0.13, 0.08 | ” |
| s-DABNA-O-Me    | ITO/NPD/TCTA/mCP/EM/LTSPO<sub>1</sub>/LiF/Al | 29.5/26.9 | 24.6 | – | 465/23 | 0.13, 0.11 | [67] |
| m-s-DABNA       | ITO/HATCN/TAPc/DCDPA/EML/DBFPO/TPBi/LiF/Al | 36.4/– | 32.1 | – | 471/18 | 0.12, 0.12 | [98] |
| 4F-s-DABNA      | ”                          | 35.8/– | 26.8 | – | 464/18 | 0.13, 0.08 | ” |
| 4F-m-s-DABNA    | ”                          | 33.7/– | 24.9 | – | 461/18 | 0.13, 0.06 | ” |
| mBP-DABNA-Me    | ITO/HATCN/TAPc/TCTA/mCP/EM/LTSPO1/DPEPO/TmPyPB/LiF/Al | 24.3/16.0 | 24.2 | 21.3 | 468/– | – | [100] |
| BSBS-N1         | ITO/HATCN/TAPc/mCBP/EM/LPPF/B3PyPB/Lif/Al | 21.0/– | – | – | 478/25 | 0.11, 0.22 | [101] |
| B-O-dpa         | ITO/PEDOT:PSS/TAPc/TCTA/mCP/EM/LTSPO1/TPBi/LiF/Al | 16.3/– | 8.3 | – | 443/32 | 0.15, 0.05 | [102] |
| B-O-Cz          | ”                          | 13.4/– | 20.3 | – | 481/63 | 0.13, 0.22 | ” |
| B-O-dmAc        | ”                          | 16.2/– | 23.1 | – | 475/44 | 0.12, 0.21 | ” |
| B-O-dpAc        | ”                          | 17.0/– | 22.8 | – | 473/42 | 0.12, 0.20 | ” |
| CzBN0           | ITO/HATCN/TAPc/TCTA/mCP/EM/LTSPO1/POT2T/ANT-BIZ/LiF/Al | 13.6/5.0 | 14.7 | – | 454/36 | 0.14, 0.08 | [103] |
| DMAcBN0         | ”                          | 20.4/8.6 | 31.2 | – | 472/41 | 0.13, 0.19 | ” |
| DPacBN0         | ”                          | 23.0/9.1 | 28.0 | – | 468/37 | 0.13, 0.14 | ” |
| tCBNDADPO       | ITO/MoO<sub>3</sub>/mCP/EM/DBDPOPO/LiF/Al | 30.8/16.2 | 47.1 | 45.5 | 472/28 | 0.14, 0.22 | [104] |
| tDABNA-dtB      | ITO/HATCN/TAPc/EML/HTL/DBL/ETL/Liq/Liq/Liy/Al | 11.4/10.9 | 9.7 | – | 471/22 | 0.11, 0.13 | [105] |
| SF1-BN          | ITO/HATCN/TAPc/TCTA/mCP/EM/LTSPO1/DPEPO/TmPyPB/LiF/Al | 35.9/14.0 | 70.0 | 56.7 | 492/27 | 0.07, 0.47 | [106] |
| SF3-BN          | ”                          | 31.7/12.7 | 60.0/24.1 | 46.6/12.0 | 492/28 | 0.08, 0.44 | ” |
| FN1             | ITO/HATCN/TAPc/TCTA/mCP/EM/DBDPO/ANT-BIZ/LiF/Al | 31.2/9.3 | 20.9/– | 14.9/– | 457/28 | 0.14, 0.08 | [95] |
| BN2             | ”                          | 33.2/15.5 | 29.7/– | 20.3/– | 467/23 | 0.13, 0.11 | ” |
| BN3             | ”                          | 37.6/26.2 | 27.5/– | 19.0/– | 458/23 | 0.14, 0.08 | ” |
| DPACzBN1        | ITO/HATCN/TAPc/TCTA/mCP/EM/LTSPO1/POT2T/ANT-BIZ/LiF/Al | 23.6/9.6 | 36.0/– | – | 475/34 | 0.14, 0.30 | [107] |
| DPACzBN2        | ”                          | 24.0/14.3 | 31.6/– | – | 469/28 | 0.13, 0.16 | ” |
| DPACzBN3        | ”                          | 27.7/6.7 | 34.5/– | – | 472/24 | 0.12, 0.18 | ” |
| PTZBN1          | ”                          | 26.9/17.9 | 69.9/– | 49.9/– | 496/47 | 0.16, 0.51 | [108] |
| PTZBN2          | ”                          | 30.5/23.0 | 59.6/– | 46.8/– | 483/43 | 0.13, 0.31 | ” |
| PTZBN3          | ”                          | 19.9/12.1 | 30.6/– | 24.0/– | 476/36 | 0.13, 0.22 | ” |
devices of the compounds were fabricated in DBFPO host and achieved decent performance. In the series, B-O-dpa exhibited best performance with $\text{EQE}_{\text{max}} \approx 16.3\%$ and $\text{CIE}(x,y) \approx (0.15, 0.05)$. Further, Yang et al. adopted similar design strategy as discussed above for developing three new blue MR-TADF emitters, CzBNO, DMAcBNO, and DPacBNO.\cite{103} The materials exhibited blue emission with narrow FWHM. All the compounds displayed prominent TADF property due to virtual of the opposite resonance effect of B, N, and O atoms. The OLEDs constructed using these materials as dopants exhibited $\text{EQE}_{\text{max}}$ of 13.6%, 20.4%, and 23.0% for CzBNO, DMAcBNO, and DPacBNO, respectively. Further, the EQE of acridine-containing materials DMAcBNO and DPacBNO were improved to 29.6% in TADF-sensitized devices.

Huang et al. modified the t-DABNA with 3,6-di-tert-butylcarbazole donor (TBN-TPA) at para-position of central phenyl unit relative to the B to improve the PL and EL performance.\cite{74} The distinguished absorption profiles of DABNA-1 and TBN-TPA indicate the involvement of appended carbazole in the electronic transitions. The solution PL of TBN-TPA showed a 20 nm redshifted emission compared to DABNA-1 with a broad FWHM of 26 nm. The mCBP-doped film of TBN-TPA displayed improved PLQY (97%) compared to DABNA-1 (88%) attributed to its high oscillator strength. Also, TBN-TPA witnessed improved $\Delta E_{\text{ST}}$ and $\tau_4$ and $k_{\text{RISC}}$ because of the increased CT with the aid of an electron-rich carbazole donor. The OLEDs were fabricated using 4 wt% of TBN-TPA in 26DCzPPy host and demonstrated $\text{EQE}_{\text{max}}$ of 32.1% and CE of 40.2 cd A$^{-1}$. The EL spectra of TBN-TPA displayed narrow FWHM $\approx 27$ nm and $\text{CIE}(x,y)$ of (0.12, 0.19). This performance is much superior than DABNA-1, though the device stack is different. Further, TBN-TPA was used as a host for the yellow Ir-phosphor and exhibited low $V_{\text{on}}$ of 3.0 V together with a high $I_{\text{max}}$ of 30.339 cd m$^{-2}$ and $\text{EQE}_{\text{max}}$ of 22.2%. However, the reported chemical structure was misinterpreted, which was further confirmed by Hatakeyama et al.\cite{65} (vide infra).

Further, Wang et al. reported a peripheral cladding strategy by introducing diphenylamine and tert-butyl substituents on DABNA-1 to improve the PL and EL efficiencies and suppress the concentration quenching. They designed and synthesized three emitters named PAB, 2iPAB, and 3iPAB.\cite{99} The t-Bu-substituted derivatives 2iPAB ($\lambda_{\text{PL}} \approx 456$ nm) and 3iPAB ($\lambda_{\text{PL}} \approx 456$ nm) showed 6 nm redshifted emission in toluene compared to PAB ($\lambda_{\text{PL}} \approx 449$ nm). At the same time, t-Bu units effectively protected aggregation-caused redshift in film state, as evident from their negligible bathochromic shift from solution to film. The compound showed a narrow FWHM of 23–26 nm and moderate PLQY of 60–74%. Also, they displayed short $\tau_4$ (55–74 $\mu$s) than DABNA-1 due to their improved $\Delta E_{\text{ST}}$ (0.06–0.1 eV). As expected, the PAB, 2iPAB, and 3iPAB showed deep-blue $\lambda_{\text{EL}}$ nm/FWHM (nm)/CIE($x,y$) of 456/31/(0.14, 0.07), 456/27/(0.14, 0.07), 460/26/(0.14, 0.07), respectively. The $\text{EQE}_{\text{max}}$ (%)$/\text{CE (cd/A)}/\text{PE (lm/W)}$ are of 14.7/10.4/7.1 for PAB, 16.8/11.8/8.0 for 2iPAB, and 19.3/13.4/10.2 for 3iPAB. These results indicate that the peripheral protection of narrow-band TADF emitters with t-Bu units can help to improve the device performance.

Hatakeyama et al. developed a series of MR-TADF chromophores (B2-B4) containing double or triple B-atoms with extended conjugated skeleton of DABNA, which was accomplished by the one-shot borylation reaction.\cite{74} The photophysical properties were investigated in 1 w% PMMA-doped films. The $\lambda_{\text{PL}}$ (nm) of B2, B2-F, B3, and B4 is 455, 467, 441, and 450 nm, respectively. The observed redshift ($\approx 17$ nm) with broad FWHM of 44 nm for B2-F compared to B2 was attributed to the electron-withdrawing F atom in the former. Although B3 showed deep-blue emission, it displayed relatively low PLQY (33%). The compounds B2 and B3 revealed low $\Delta E_{\text{ST}}$ of 0.15 and 0.19 eV, which is sufficient to accomplish efficient RISC. The authors explored the applicability of B2 as an emitter in an OLED and found to exhibit $\text{EQE}_{\text{max}}$ of 18.3% and CE of 11.5 cd A$^{-1}$. However, its EL displayed 5 nm redshift compared to PL with broad FWHM $\approx 37$ nm, which resulted in $\text{CIE}(x,y)$ of (0.13, 0.11).

To expand the chemical space of MR-TADF emitters, in 2021, Yasuda et al. reported a ternary (B/N/S)-doped MR-TADF framework and designed an acyclic emitter, BSBS-N1.\cite{104} The two S atoms in the phenothiaborin subunits of BSBS-N1 are expected to induce the MR effect with N atoms due to its electron richness and facilitate the RISC owing to the heavy atom effect. It displayed sky-blue emission with $\lambda_{\text{PL}}$ of 473 FWHM of 21 nm. The BSBS-N1 revealed a small stoke shift of 15 nm owing to the reduced structural reorganizations in the excited state due to its fully fused molecular geometry. The estimated $S_{1}/T_1$/$\Delta E_{\text{ST}}$/PLQY of doped film of BSBS-N1 are 2.59 eV/2.45 eV/0.14 eV/89%. The BSBS-N1 revealed short $\tau_4$ and fast $k_{\text{RISC}}$ of 5.6 and $1.9 \times 10^6$ s$^{-1}$ due to the heavy atom effect of S. Further, its OLED exhibited sky-blue emission, $\lambda_{\text{EL}}$ of 478 nm and FWHM of 25 nm. Although BSBS-N1 showed a low $\text{EQE}_{\text{max}}$ of 21.0% compared to the typical sky-blue emitter BBCz-SB (27%), it showed improved efficiency roll-off at high brightness attributed to its fast RISC and suppressed bimolecular exciton quenching (TTA or TPA).

Kim et al. reported a new pure blue emitter named mBP-DABNA-Me, wherein xylene and meta-phenyl groups were introduced into the DABNA core to effectively suppress aggregation-caused quenching and prevent the isomer formation in the reaction.\cite{105} The mBP-DABNA-Me manifested pure blue

| Compound | Device structure | $\text{EQE}_{\text{max}}$/% | CE, cd/A | PE, lm/W | $\lambda_{\text{EL}}$/FWHM [nm] | $\text{CIE}(x,y)$ | References |
|----------|-----------------|--------------------------|----------|----------|-----------------------------|----------------|------------|
| CzBO     | ITO/HATCN/TAPC/mMCP/EMI/PFF/B3PyPB/LiF/Al | 13.4/-     | 7.4/-   | 5.7/-   | 448/30                  | 0.15,0.05     | [109]      |
| CzB     | "              | 23.1/-     | 25.8/-  | 19.4/-  | 473/31                  | 0.11,0.16     | "          |
| CzBe    | "              | 23.9/-     | 34.8/-  | 25.8/-  | 483/33                  | 0.10,0.24     | "          |

Table 2. Continued.
emission with $\lambda_{PL}$ of 464 nm and FWHM of 28 nm in the toluene solution. Notably, the doped film exhibited only a 3 nm redshift compared to the solution attributed to the suppressed $\pi-\pi$ interactions, and as a result, the PLQY yielded in 97%. The OLED fabricated using mBP-DABNA-Me demonstrated EQEmax of 24.3% and CE of 24.2 cd A$^{-1}$ with pure blue emission (468 nm). Interestingly, the color purity of mBP-DABNA-Me was unchanged even at above 20 wt% doping concentration, highlighting the importance of the bulky substituent addition strategy for effective suppression of aggregation-caused emission quenching.

Xu et al. reported self-host featured MR-TADF emitter, namely, tCBNDADPO, by integrating MR-core (tCBN) with the ambipolar host segment (DADPO) (Chart 2).[104] Notably, the tCBNDADPO displayed improved TADF properties with accelerated $k_r \approx 2.11 \times 10^8$ s$^{-1}$ and suppressed $k_{nr}$. Also, tCBNDADPO manifested narrowband blue emission with FWHM $\approx$ 28 nm even at high doping concentration of 30 wt%. Further, the nondoped OLED demonstrated an EQEmax of 30% attesting the superiority of self-host strategy in constructing the efficient host-free MR-TADF emitters.

In 2022, Lee et al. reported MR-TADF blue emitter (t-DABNA-dtB) by introducing di-tert-butyl benzene substituent in the MR core (t-DABNA) to minimize the quenching mechanisms by restricting the intermolecular interaction.[105] The designed emitter showed a high PLQY and small FWHM $\approx 22$ nm, which realized high EQE of 11.4% in the single unit OLED with operational lifetime LT95 of 208 h at 1000 cd m$^{-2}$ and over 10 000 h at 100 cd m$^{-2}$. The t-DABNA-dtB displayed pure blue emission $\lambda_{EL} \approx 470$ nm with a CIEy coordinate of $\approx 0.13$. The optimized tandem device of the new blue emitter achieves a high EQE $> 25\%$ and extremely long LT95 $> 500$ h at 1000 cd m$^{-2}$.

Chart 2. Chemical structures of blue MR-TADF emitters.
Notably, in the case of a tandem device, the CIE\(y\) coordinate is significantly decreased to 0.11. The lifetime of this work is one of the best reported blue OLEDs.

Generally, MR-TADF chromophores are susceptible to the aggregation-caused emission quenching because of their planar geometries. To overcome this, recently Jiang et al. reported a new design featuring the integration of spirobifluorene (SBF) building block with MR-core (SF1BN and SF3BN) either via C1 or C3 positions, respectively.\(^{[95]}\) As expected, the SBF-substituted derivatives prevented the aggregation even at high doping ratio and manifested excellent PLQY with a narrow FWHM of \(\approx 27\) nm. Particularly, the C1-substituted SBF in SF1BN acts as a shield to prevent aggregation at high doping ratios compared to the parent molecule and SF3BN. Compared to the parent core, the designed emitters showed 1.5 times increased EQE (32.5–35\%). These results indicate that the spirostrategy is an effective method for preventing the aggregation-caused emission quenching in MR-TADF emitters.

In 2022, Yang et al. reported three deep blue MR-TADF emitters (BN1, BN2, and BN3) by extending the \(\pi\)-skeleton by increasing the number of phenyl rings from 7 to 13.\(^{[95]}\) The designed emitters were synthesized by a one-pot lithium-free cyclization method. All three emitters exhibited high PLQY of over 90\%, with increased \(k_{RISC}\) from BN1 to BN3. The emitters showed a deep-blue emission with CIE\(y\) coordinate below 0.08. The OLED fabricated with BN3 exhibited a EQE\(_{\text{max}}\) of 37.6\% and improved roll-off, representing the best efficiency reported for deep-blue TADF OLEDs. These results highlight that the extinction of fused \(\pi\)-conjugated skeleton can improve the RISC and enhance the OLED performance.

The same group further reported a new approach for narrowing the EL spectra of MR-TADF emitters by peripheral decoration strategy. They developed three new MR-TADF emitters by attaching one or two diphenylamine units on the parent CzBN core (DPACzBN1, DPACzBN2, and DPACzBN3).\(^{[106]}\) Interestingly, with increasing the number of diphenylamine units, the FWHM of EL spectra decreased. In the series, the DPACzBN3 exhibited deep-blue emission with FWHM of 20 nm. Also, the diphenylamine decoration benefited to promote the PLQY and \(k_{RISC}\) of the emitters. The fabricated OLED of these compounds displayed blue to sky-blue emission. In the series, the DPACzBN3 exhibited best performance with EQE\(_{\text{max}}\) of 27.7\%.

Later, same group strategically developed three new blue emitters, PTZBN1, PTZBN2, and PTZBN3.\(^{[108]}\) By virtue of peripheral modification with diphenylamine donor units, the emission wavelengths of the compounds were tuned from 490 nm (PTZBN1) to 468 nm (PTZBN3). The incorporation of sulfone functionality in PTZBN3 benefited to restrict the emission in deep-blue region with high PLQY of 98\% and narrowband emission, FWHM of 30 nm. In the series, the PTZBN2-based device exhibited EQE of 34.8\%. Impressively, the PTZBN3-based device demonstrated high EQE \(\approx 32.0\%\) in deep-blue region (\(\lambda_{\text{EL}} \approx 468\) nm) indicates the importance of sulfone modification in the development of efficient deep-blue MR-TADF emitters.

As mentioned above, \(k_{RISC}\) associated with spin-flip from \(T_1 \rightarrow S_1\) is a rate limiting factor in the TADF emitters. To promote the \(k_{RISC}\) in MR-TADF emitters, Yasuda et al. proposed a heavy atom doping approach and consequently they developed three blue MR-TADF emitters by doping the different heteroatoms (O, S, and Se), viz., CzBO, CzBS, and CzBSe.\(^{[109]}\) With the aid of prominent MR-effect, the compounds showed low \(\Delta E_{\text{ST}}\) below 0.15 eV. Further, the SOC of the compounds improved from O to Se attributed to the heavy atom effect of Se. In the series, CzBSe displayed ultrafast \(T_1 \rightarrow S_1\) exciton upconversion with high \(k_{RISC}\) rate exceeding \(10^8\) s\(^{-1}\), which is higher than its \(k_r\). Even the \(k_{RISC}\) of CzBSe is accelerated by 20 000 and 800 times than the O- and S-doped emitters, respectively (Figure 4). As a result, the CzBSe demonstrated best OLED performance with EQE\(_{\text{max}}\) of 23.9\% and CIE\(y\) \(\approx 0.24\). In 2019, Hatakeyama et al. developed an expanded DABNA-based linear conjugated MR-TADF emitter consisting of four benzene rings containing two B and four N atoms and two peripheral diphenylamine groups, \(\nu\)-DABNA (Chart 3).\(^{[94]}\) Intriguingly, the \(\nu\)-DABNA showed a narrow FWHM of 14 nm in solution, which is the narrowest FWHM reported so

Figure 4. Design approach for accelerating \(k_{RISC}\) of the MR-TADF emitters.
far for MR-TADF emitters. In the same report, the authors also developed a new DOBNA-based host material named DOBNA-OAr. The 1 wt% ν-DABNA-doped DOBNA-OAr films exhibited λPL of 469 nm, PLQY of 90%, and ΔEST of 0.017 eV, which is the smallest among the reported MR-TADF emitters. The ν-DABNA also exhibited a high kRISC of 2.0 × 10^5 s⁻¹, which is 3 times higher than the reported DABNA-1 and DABNA-2,[62] attributed to its low ΔEST. The OLED demonstrated ultrapure blue emission with λEL of 469 nm and FWHM of 18 nm, and CIE(x,y) of (0.12, 0.11). In addition, the device displayed excellent performance with EQEmax of 34.4% at 15 cd m⁻² and a suppressed efficiency roll-off of 26.6% at 1000 cd m⁻². This is attributed to the reduced bimolecular exciton quenching with the aid of small ΔEST.

Although ν-DABNA exhibited excellent TADF property, narrow FWHM, and high efficiency, its emission restricted to the sky-blue emission, λPL ≈ 469 nm, and deviated its CIEY coordinate ≈0.11 from the NTSC/ITU BT.2020 standards. To address this, same group has proposed a new molecular design by replacing the N-atom with the O in the ν-DABNA core, yielded ν-DABNA-O-Me.[67] They envisaged that, because of the low atomic energy of O atom, it restricts the π-conjugation of the HOMO rather than LUMO orbital. As expected, the HOMO energy level of ν-DABNA-O-Me showed a large deviation (≈0.16 eV) than LUMO energy (≈0.13 eV), leading to the wide bandgap for the former. The photophysics was analyzed in 1 wt% emitter-doped PMMA film, and ν-DABNA-O-Me displayed 5 nm blueshifted emission compared to ν-DABNA. However, its FWHM (24 nm) was broadened compared to the ν-DABNA. Further, the OLED fabricated using ν-DABNA-O-Me demonstrated decent performance with EQEmax of 29.5% and CE of 24.6 cd A⁻¹. Notably, ν-DABNA-O-Me displayed alleviated efficiency roll-off only 2.6% at 1000 cd m⁻² compared to ν-DABNA (8.4%) may be due to the reduced bimolecular quenching process. Also, ν-DABNA-O-Me exhibited an improved device lifetime, LT₅₀, of 314 h.

Chart 3. Chemical structures of ν-DABNA derived blue MR-TADF emitters.

Figure 5. Design strategy for constructing efficient deep-blue MR-TADF emitters.
compared to \( \nu \)-DABNA of 31 h at 100 cd m\(^{-2}\). Nonetheless, as per the design, \( \nu \)-DABNA-O Me exhibited improved color purity with CIE\( y \) of 0.10 compared to \( \nu \)-DABNA. However, this CIE\( y \) is still unsatisfactory for practical application.

To further improve the color purity of the \( \nu \)-DABNA, Yasuda and co-workers developed a new design comprised of the replacement of intracyclic N-atoms with the less electron rich O and/or S atoms, BOBO-Z, BOBS-Z, and BSBS-Z (Figure 5).\[^{[97]}\] As expected, these luminophores showed conspicuous blueshifted emission in solution in the order of BOBO-Z (\( \lambda_{\text{PL}} \approx 453 \) nm), and BSBS-Z (\( \lambda_{\text{PL}} \approx 460 \) nm) compared to \( \nu \)-DABNA with retaining narrow FWHM of 15–21 nm. The calculated CIE\( (x,y) \) of BOBO-Z (0.15, 0.03), BOBS-Z (0.15, 0.06), and BSBS-Z (0.14, 0.07) is encouraged as they are closely matched with the requirement of standard UHD displays. Even the 3 wt% mCBP-doped films of BOBO-Z, BOBS-Z, and BSBS-Z showed deep-blue emission with a maximum of \( \lambda_{\text{PL}} \approx 445, 457, \) and 464 nm, respectively, compared to \( \nu \)-DABNA of \( \lambda_{\text{PL}} \approx 474 \) nm. The S-containing derivatives, BOBS-Z (\( k_{\text{RISC}} \approx 8.6 \times 10^4 \text{ s}^{-1} \)) and BSBS-Z (\( k_{\text{RISC}} \approx 1.6 \times 10^5 \text{ s}^{-1} \)), displayed 2.4 and 4.2 times faster \( k_{\text{RISC}} \) than the \( \nu \)-DABNA (\( 3.3 \times 10^4 \text{ s}^{-1} \)) may be attributed to their heavy atom effect of S, which is also supported by the DFT computations. Later, the applicability of these materials as dopants in OLEDs was tested in mCBP host. Consistent with their PL, the EL of the compounds showed deep-blue emission, 445 nm for BOBO-Z, 456 nm for BOBS-Z, and 463 nm for BSBS-Z, and narrow FWHM falls in the range of 18–23 nm, which indicates distinct hypsochromic shift compared to the \( \nu \)-DABNA (472 nm). Consequently, OLEDs displayed excellent color purity with CIE\( (x,y) \) of (0.15, 0.04) for BOBO-Z, (0.14, 0.06) for BOBS-Z, and (0.13, 0.08) for BSBS-Z fulfilling the requirements of Rec.2020 standard of UHD OLEDs. The S-containing derivatives BOBS-Z and BSBS-Z exhibited best performance with EQE\( \text{max} \) of 26.9% and 26.8% over BOBO-Z (13.6%) and \( \nu \)-DABNA (26.6%).

Initially, the device stability was analyzed in unipolar host, mCBP and showed a very short lifetime; further, it was improved (LT\(_{50} > 30 \) h at 100 cd m\(^{-2}\)) by replacing the mCBP with bipolar host mCBP-CN.

In 2020, Naveen et al. reported a new molecular design for the blue-shift of \( \nu \)-DABNA by introducing an electron-donating methyl and electron-withdrawing F units on para- and ortho-positions relative to the B-atom, respectively.\[^{[98]}\] The authors expected that the weak electron-donating methyl units placed para- to B-atom in m\(-\)DABNA can weaken the electron-withdrawing nature of B and upshift the LUMO energy while increasing optical bandgap compared to \( \nu \)-DABNA. Similarly, the weak electron-withdrawing F atom reduces the electron donating strength of N-atom, which destabilize the HOMO energy without effecting on the LUMO energy. Subsequently, 4F-m\(-\)DABNA displayed hypsochromic shift compared to \( \nu \)-DABNA; the DFT computations also support this hypothesis. Electrochemical studies revealed the improved optical bandgap for the m\(-\)DABNA (2.62 eV), 4F\(-\)DABNA (2.63 eV), and 4F-m\(-\)DABNA (2.65 eV) compared to \( \nu \)-DABNA of 2.60 eV. As expected, the compounds m\(-\)DABNA, 4F\(-\)DABNA, and 4F-m\(-\)DABNA showed deep-blue emission in toluene solution with \( \lambda_{\text{PL}} \) of 464, 457, and 455 nm, which is 4–11 nm hypsochromic shift than the \( \nu \)-DABNA. Interestingly, the F and methyl substitutions did not affect the FWHM of the emitters, which indicates that it is a promising strategy to develop pure deep-blue emitters. The calculated \( \Delta E_{\text{ST}}/\tau_k/\text{RISC} \) of m\(-\)DABNA, 4F\(-\)DABNA, and 4F-m\(-\)DABNA are 0.07 eV/3.09 \( \mu \)s/2.30 \( \times \) \( 10^3 \) s\(^{-1}\), 0.05 eV/3.12 \( \mu \)s/2.28 \( \times \) \( 10^3 \) s\(^{-1}\), and 0.07 eV/3.39 \( \mu \)s/2.10 \( \times \) \( 10^3 \) s\(^{-1}\), respectively. The observed \( k_{\text{RISC}} \) of the compounds in DPEPO film is relatively higher than the \( \nu \)-DABNA, indicating their promising nature as TADF emitters. The compounds restored the pure blue EL/narrow FWHM of 471/18 nm for m\(-\)DABNA, 464/18 nm for 4F\(-\)DABNA and 461/18 nm for 4F-m\(-\)DABNA. Consequently, the 4F\(-\)DABNA and 4F-m\(-\)DABNA showed excellent color purity with CIE\( (x,y) \) of (0.13, 0.08) and (0.13, 0.06) respectively. Also, the 4F\(-\)DABNA and 4F-m\(-\)DABNA achieved superior EQE\( \text{max} \) of 35.8% and 33.7%, which is either superior or comparable to the \( \nu \)-DABNA. Thus, the proposed design strategy is promising for developing high-efficiency deep-blue emitters with EQE > 35%.

In 2020, Colman et al. developed a new ladder-type B,N-containing heptacene (3BNOH), and studied its photophysical properties.\[^{[99]}\] The compound showed violet emission in toluene solution with \( \lambda_{\text{PL}} \) of 390 nm, a small FWHM of 31 nm, and PLQY of 50%. 3BNOH displayed a large \( \Delta E_{\text{ST}} \) of 0.31 eV in solution, which is larger than the reported MR-TADF emitters. The temperature dependent PL study suggests the formation of aggregates in the THF matrix, which induced delayed fluorescence from the TTA channel. However, the TADF component is dominant at a high temperature, 300 K. The direct calculated activation energy for delayed emission was 70 meV, and its \( \Delta E_{\text{ST}} \) is 0.31 eV. This may be due to the contribution of higher triplets for the RISC, which is evident by the DFT studies. In 1 wt% PMMA film, 3BNOH exhibited 5 nm redshifted emission and FWHM of 32 nm, and its \( \Delta E_{\text{ST}} \) became narrow by 0.22 eV compared to the solution. Interestingly, it showed impressive CIE\( y \approx 0.01 \) in the PMMA matrix. But the delayed lifetime in the film state (260 \( \mu \)s) was longer than the solution state (0.45 \( \mu \)s). The activation energy in the film state matches with the \( \Delta E_{\text{ST}} \) indicating that the high lying triplet contribution for RISC in the film state is negligible.

Hatakeyama et al. developed an expanded helicene-type MR-TADF emitters consisting of three B and six nitrogen atoms (\( \nu \)-DABNA-Mes) employing a one-shot triple borylation reaction.\[^{[196]}\] The PL and EL performance of \( \nu \)-DABNA-Mes were compared with the reference material \( \nu \)-DABNA. The 1 wt% dispersed PMMA films showed sharp emission at 484 nm with a narrow FWHM of 16 nm, which was redshifted compared to the parent core due to the extended \( \pi \)-skeleton. As a result of extended \( \pi \)-conjugation, the \( \nu \)-DABNA-Mes showed an improved MR effect and resulted in a narrow \( \Delta E_{\text{ST}} \) of 0.005 eV, short \( \tau_d \) of 2.4 \( \mu \)s, and fast \( k_{\text{RISC}} \) of 4.4 \( \times \) \( 10^4 \) s\(^{-1}\) compared to the \( \nu \)-DABNA core. Further, the applicability of \( \nu \)-DABNA-Mes was examined in solution-processed OLED in a polymer host. The device exhibited sky blue emission with narrow emission FWHM of 27 nm, \( \lambda_{\text{EL}} \) of 480 nm, and CIE\( (x,y) \) of (0.09, 0.21). In addition, the \( \nu \)-DABNA-Mes demonstrated an EQE\( \text{max} \) of 22.9%, CE of 26.7 cd A\(^{-1}\), but it displayed severe efficiency roll-off at 1000 cd m\(^{-2}\) with EQE of 10.9%, and CE of 12.9 cd A\(^{-1}\) was attributed to the binuclear quenching of triplet excitons via TTA or TSA process.
Chart 4. Chemical models of the green MR-TADF emitters.
Table 3. Physicochemical properties of green, orange-red, and full-color MR-TADF emitters.

| Compound | \( \lambda _{\text{ex}} \) [nm] (sol/film) | FWHM (sol/film) | \( \Phi _{T} \) (sol/film), [%] | \( S_{1}/T_{1}/\Delta E_{\text{TADF}} \) [eV] | \( r_{p} \) [ns] \( r_{t} \) [\( \mu \text{s} \)] | References |
|----------|----------------|--------------|----------------|-----------------|----------------|----------------|
| 2F-BN    | 494/--        | 26/--        | 95/88          | 2.51/2.35/0.16 | --/25.9        | [78]           |
| 3F-BN    | 499/--        | 37/--        | 90/83          | 2.48/2.40/0.08 | --/16.7        |                |
| 4F-BN    | 496/--        | 26/--        | 98/91          | 2.50/2.39/0.11 | --/19          |                |
| AZA-BN   | 522/527       | 28/36        | --/94          | 2.37/2.19/0.18 | 13.4/164       | [79]           |
| DibKPhCzB | 496/503     | 21/30        | --/97          | 2.59/2.50/0.09 | --/61.3        | [76]           |
| m-Cz-BNCz | 519/521     | 38/39        | --/97          | 2.50/2.42/0.08 | --             | [77]           |
| S-Cz-BN  | 490/--        | 23/--        | 94/--          | --              | 5.6/69.6       | [110]          |
| A-Cz-BN  | 490/--        | 22/--        | 98/--          | --              | 5.8/76.0       |                |
| BN-CP1   | 490/496       | 23/25        | --/93          | 2.63/2.51/0.12 | 5.1/79.6       | [111]          |
| BN-CP2   | 490/496       | 23/26        | --/91          | 2.62/2.49/0.13 | 5.0/83.6       |                |
| BBCz-DB  | 446/--        | 16/--        | 93/--          | 2.74/2.59/0.15 | 4.5/86         | [80]           |
| BBCz-SB  | 489/--        | 23/--        | 98/--          | 2.63/2.48/0.15 | 4.7/102        |                |
| BBCz-G   | 517/--        | 34/--        | 90/--          | 2.50/2.36/0.14 | 5.0/17         |                |
| BBCz-Y   | 549/--        | 42/--        | 85/--          | 2.41/2.27/0.14 | 5.6/29         |                |
| BBCz-R   | 615/--        | 21/--        | 89/--          | 2.09/1.90/0.19 | 6.1/89         |                |
| Cz-b     | 460/461       | 23/30        | 83/89          | 2.70/2.58/0.12 | 5.0/39.0       | [71]           |
| Cz-B     | 477/484       | 25/30        | 98/97          | 2.60/2.46/0.14 | 5.2/106        |                |
| TCz-B    | 512/517       | 27/31        | 100/89         | 2.42/2.33/0.09 | 5.4/60         |                |
| DACA-B   | 572/576       | 34/44        | 87/87          | 2.17/2.03/0.14 | 7.9/316        |                |
| DPTRZ    | 521/--        | 24/--        | 94/--          | 2.33/2.15/0.18 | 13.1/78        | [112]          |
| TPTRZ    | 501/--        | 27/--        | 97/--          | 2.44/2.33/0.11 | 8.7/83.5       |                |
| Ppm      | 499/--        | 25/--        | 96/--          | 2.43/2.32/0.11 | 8.3/86.5       |                |
| CNpm     | 515/--        | 36/--        | 93/--          | 2.28/2.13/0.15 | 14.2/52        |                |
| NBO      | 487/--        | 27/--        | 92/--          | 2.55/2.43/0.12 | 6.7/5.9        | [113]          |
| NBNP     | 500/--        | 29/--        | 93/--          | 2.48/2.39/0.09 | 7.6/3.8        |                |
| BN-TP    | 523/--        | 34/--        | 96/--          | 2.48/2.33/0.14 | 7.1/44.0       | [114]          |
| TW-BN    | 486/485       | 21/--        | 56/92          | 2.62/2.50/0.12 | 2.9/112        | [115]          |
| Tph-BN   | 492/495       | 22/--        | 91/94          | 2.59/2.50/0.09 | 4.9/62         |                |
| pCz-BN   | 491/496       | 20/--        | 90/95          | 2.62/2.47/0.15 | 4.1/89         |                |
| mCz-BN   | 495/494       | 21/--        | 85/88          | 2.26/2.42/0.14 | 6.7/95         |                |
| BN1      | 496/499       | 23/38        | 99/93          | 2.50/2.39/0.11 | 6.2/68.6       | [116]          |
| BN2      | 534/538       | 30/41        | 98/89          | 2.32/2.19/0.13 | 7.1/107        |                |
| BN3      | 562/563       | 30/44        | 98/86          | 2.23/2.14/0.09 | 6.3/127        |                |
| BN-ICz-1 | 516/--        | 21/--        | 99.2/--        | 2.38/2.16/0.22 | 6.4/342        | [117]          |
| BN-ICz-2 | 516/--        | 22/--        | 98.3/--        | 2.38/2.20/0.18 | 6.7/48.6       |                |
| OAAB-ABP-1 | 506/--   | 34/--        | 90/--          | --/--/0.12     | 9.9/32         | [64]           |
| DMAc-BN  | 484/--        | 33/--        | 88/--          | --/--/0.16     | 6.2/32.9       | [118]          |
| PKZ-BN   | 502/--        | 38/--        | 90/--          | --/--/0.17     | 8.2/90.7       |                |
| TPXZBN   | 502/--        | 33/--        | 91/99          | --/--/0.16     | 7.4/27         | [119]          |
| DPPXZBN  | 500/--        | 32/--        | 90/94          | --/--/0.13     | 10/15          |                |
| BN-DMAC  | 485/--        | 29/--        | 63/--          | --/--/0.14     | 5.1/13.9       | [72]           |
| BN-DPAC  | 490/--        | 30/--        | 86/--          | --/--/0.11     | 4.4/11.6       |                |
| 2PXZBN   | 504/515       | 34/40        | 78/84          | 2.57/2.39/0.18 | 6.8/25.3       | [82]           |
| 2PTZBN   | 510/519       | 39/44        | 58/80          | 2.53/2.39/0.14 | 4.8/16.1       |                |
| SBON     | 463/--        | 24/--        | 74/--          | 2.68/2.52/0.16 | 9.2/11.5       | [120]          |
| SBSN     | 489/--        | 27/--        | 76/--          | 2.54/2.44/0.10 | 8.9/32         |                |
| DBON     | 505/--        | 20/--        | 98/--          | 2.46/2.33/0.13 | 3.7/24         |                |
Table 3. Continued.

| Compound          | \( \lambda_{PL} \) [nm] | \( \Phi_m \) (sol/film), [%] | \( \frac{S_i/T_i}{\Delta E_{ST}} \) [eV] | \( \tau_s \) [ns] | \( \tau_e \) [ns] | References |
|-------------------|--------------------------|-------------------------------|--------------------------------|------------------|------------------|------------|
| DBSN              | 553/–                     | 98/–                          | 2.56/2.38/0.18                  | 8.2/28.1         | ±                | [124]      |
| R-BN              | 662/672                   | 100/–                         | 1.85/1.69/0.11                  | 12/16            | ±                | [71]       |
| R-TBN             | 692/698                   | 96/–                          | 1.79/1.63/0.16                  | 14.2/46          | ±                | [121]      |
| BNO1              | 605/610                   | 32/35                         | 2.11/1.85/0.26                  | ±                | ±                |           |
| BNO2              | 609/618                   | 95/–                          | 2.13/1.86/0.27                  | ±                | ±                |           |
| BNO3              | 616/624                   | 96/–                          | 2.11/1.85/0.26                  | ±                | ±                |           |
| CNC6BNCz          | 581/582                   | 90/96                         | 2.28/2.10/0.18                  | 77/60            | ±                | [70]       |
| (R)-OBN-2CN-BN    | 493/–                     | 99/95                         | 2.47/2.35/0.12                  | 9.8/95.3         | ±                | [68]       |
| (R)-OBN-4CN-BN    | 500/–                     | 96/90                         | 2.46/2.33/0.13                  | 10/97.4          | ±                |           |
| BN1               | 502/–                     | 61/–                          | –/–/0.02                       | 6.19/–           | ±                | [122]      |
| BN2               | 475/–                     | 88/–                          | –/–/0.02                       | 6.39/–           | ±                |           |
| BN3               | 511/–                     | 72/–                          | –/–/0.16                       | 4.8/16.2         | ±                |           |
| BN4               | 500/522                   | 88/96                         | –/–/0.14                       | 5.1/8.2          | ±                |           |
| BN5               | 497/512                   | 87/92                         | –/–/0.14                       | 5.1/23.1         | ±                |           |
| (P/M)-Helicene-BN | 520/–                     | –/–                           | 2.56/2.38/0.18                  | 5.0/71           | ±                | [123]      |
| BN-MelAc          | 497/–                     | –/–                           | –/–/0.11                       | 8.2/28.1         | ±                |           |

3. Green MR-TADF Emitters

As discussed above, the DABNA-based MR-TADF emitters flourished with very high EQE and narrowband emission; however, they are limited to the blue region. Nonetheless, it is highly desirable to develop full-color emitters especially ultrapure primaries, i.e., green and red, for fabricating wide color gamut UHD displays. To address this, Duan et al. replaced the diphenylamine unit in the DABNA core with the rigid ditet-butylcarbazole and substituted the resultant MR-TADF core (BCz-BN) with either carbazole donor or fluorobenzene acceptor on para-carbon of central phenyl unit relative to the B-atom yielded a series of green MR-TADF emitters (Chart 4). 2F-BN, 3F-BN, 4F-BN, and TCz-BN. In substitution of fluorobenzene fragment stabilized the LUMO energy and depressed the bandgap, which resulted bathochromic-shifted emission. These emitters manifested high PLQY of 99–99% in toluene and exhibited green emission \( \lambda_{EL} \approx 501–503 \text{ nm} \) with narrow FWHM of 22–25 nm. The \( \Delta E_{CT} (\text{eV})/\tau_0 (\mu\text{s}) \) of 2F-BN, 3F-BN, and 4F-BN are of 0.16/25.9, 0.08/16.7, and 0.11/19.0, respectively (Table 3). The \( \tau_0 \) of these compounds is shorter than the TCz-BN. When applied, these materials as dopants in MCPCB:35% 5TCzCB host, all the compounds showed green emission with \( \lambda_{EL}/\text{FWHM} \) of 501/40 nm for 2F-BN, 499/39 nm for 3F-BN, and 493 nm/32 nm for 4F-BN. The OLED of 2F-BN demonstrated pure green emission with \( \text{CIE}(x,y) \approx 0.25 \text{ and } 0.70 \). But the doped film exhibited a slightly broad FWHM \approx 36 \text{ nm}. The transient PL analysis indicates a relatively long \( \tau_d \) of 163 \mu\text{s} and a slow \( k_{RISC} \approx 7.53 \times 10^3 \text{ s}^{-1} \). Further, its potential as an emitter in OLED was tested in phosphorescence-sensitized MR-TADF device. The device showed low \( V_{on} \) of 2.6 \text{ V}, pure green emission of \( \lambda_{EL} \approx 528 \text{ nm} \), FWHM of 30 nm, and \( \text{CIE}(x,y) \) of (0.25, 0.70). The device exhibited \( \text{EQE}_{\text{MAX}}/\text{PE} \approx 28.25/121.7 \text{ lm W}^{-1} \) and maintained stable efficiency of 26.5% and 19.1% at 100 and 1000 cd m\(^{-2} \), respectively.

Later, Wang and co-workers developed a series of green MR-TADF emitters by modifying the para-carbon of the central phenyl unit w.r.t. to the B atom with various electron-withdrawing units (DPRZT, TPTRZ, PPh, CNPm). It is expected that the substitution of acceptor units at the para-carbon of the B atom can significantly depress the LUMO energy with negligible effect on the HOMO energy, which would narrow the bandgap and with hybridized MR and ICT (HMCT) effect are feasible to construct efficient MR-TADF emitters with tunable emission colors.

Inspired by the above report, the same group was developed another molecular design based on MR core fused with a difficult to access azo-aromatic skeleton, which can contribute to the MR effect. The target material AZA-BN was synthesized in a one-shot multiple cyclization method. To understand electronic properties and validate the HMCT concept, the authors presented the DFT computations of the model compounds. The addition of a fused aza cyclic system to the MR-core increased the extension of \( \pi \)-conjugation. It improved the HOMO/LUMO orbital distribution, which strengthen the ICT character and benefited to stabilize the S\(_2\) energy. The S\(_2\) energy is effectively modulated by the HMCT design without affecting the FWHM and oscillator strength. As expected, AZA-BN showed pure green emission with \( \lambda_{PL} \approx 522 \text{ nm} \) and narrow FWHM of 28 nm in toluene, and it was restored in 4 wt% emitter-doped mCBP film, \( \lambda_{PL} \approx 528 \text{ nm} \) with CIE\((x,y)\) of (0.25, 0.70). But the doped film exhibited a slightly broad FWHM \approx 36 nm. The transient PL analysis indicates a relatively long \( \tau_d \) of 163 \mu\text{s} and a slow \( k_{RISC} \approx 7.53 \times 10^3 \text{ s}^{-1} \). Further, its potential as an emitter in OLED was tested in phosphorescence-sensitized MR-TADF device. The device showed low \( V_{on} \) of 2.6 \text{ V}, pure green emission of \( \lambda_{EL} \approx 526 \text{ nm} \), FWHM of 30 nm, and \( \text{CIE}(x,y) \) of (0.27, 0.69). The device exhibited \( \text{EQE}_{\text{MAX}}/\text{PE} \approx 28.25/121.7 \text{ lm W}^{-1} \) and maintained stable efficiency of 26.5% and 19.1% at 100 and 1000 cd m\(^{-2} \), respectively.
| Compound | Device structure | $\text{EQE}_{\text{max}}$/(1000 cd/m$^2$), % | CE, cd/A | PE, lm/W | $\lambda_{\text{exc}}$/FWHM [nm] | CIE($x,y$) | References |
|----------|-----------------|-----------------|---------|---------|-----------------|---------|-----------|
| 2F-BN    | ITO/HATCN/NPB/BCzPh/EML/CzPhPy/ DPPyA/LiF/Al | 22/15 | – | 69.8 | 501/40 | 0.16, 0.60 | [78] |
| 3F-BN    | " | 22.7/21.1 | – | 72.3 | 499/38 | 0.20, 0.58 | " |
| 4F-BN    | " | 20.9/16.4 | – | 51.3 | 493/31 | 0.12, 0.48 | " |
| A2A-BN   | ITO/HATCN/NPB/BCzPh/EML/CzPhPy/ DPPyA/LiF/Al | 28.2/19.6 | – | 121.7 | 527/30 | 0.27, 0.69 | [79] |
| DIBuPhCzB | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 23.4/5.7 | 66.2 | 54.7 | 504/34 | 0.15, 0.61 | [76] |
| m-Cz-BNc | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 27.0/14.4 | 99.2 | 103.8 | 520/44 | 0.23, 0.69 | [77] |
| S-Cz-BN  | ITO/HATCN/NPB/BCzPh/EML/CzPhPy/ DPPyA/LiF/Al | 30.5/26.2 | – | 488/26 | 0.12, 0.43 | [110] |
| D-Cz-BN  | " | 37.2/34.3 | – | 88/24 | 0.11, 0.43 | " |
| BN-CP1   | ITO/HATCN/TAPC/TCTA/mCBP/EML/ PO-T2T/ANT-BIZ/Liq/Al | 40.0/18.5 | 83.8 | 109.7 | 496/25 | 0.09, 0.50 | [111] |
| BN-CP2   | " | 36.4/19.2 | 108.1 | 497/26 | 0.10, 0.53 | " |
| BBCz-DB  | ITO/HATCN/TAPC/mCBP/EML/PFP/ B3PyPB/LiF/Al | 29.3/– | – | 469/27 | 0.12, 0.18 | [80] |
| BBCz-SB  | " | 27.8/– | – | 487/26 | 0.09, 0.40 | " |
| BBCz-G   | " | 31.8/– | – | 515/54 | 0.26, 0.68 | " |
| BBCz-Y   | " | 29.3/– | – | 549/48 | 0.39, 0.59 | " |
| BBCz-R   | " | 22.0/– | – | 616/26 | 0.67, 0.33 | " |
| Cz-b     | " | 19.0/7.7 | 17.8 | 19.0 | 461/28 | 0.13, 0.13 | [71] |
| Cz-B     | " | 22.6/6.9 | 34.7 | 24.7 | 482/30 | 0.11, 0.31 | " |
| TCz-B    | " | 29.2/9.4 | 100.7 | 72.4 | 515/30 | 0.16, 0.71 | " |
| DACz-B   | " | 19.6/4.8 | 81.6 | 58.2 | 571/44 | 0.47, 0.51 | " |
| DPTRZ    | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 26.5/15.6 | 99.1 | 107.3 | 528/36 | 0.27, 0.60 | [112] |
| TPTRZ    | " | 30.6/15.0 | 105.8 | 116.2 | 520/41 | 0.23, 0.68 | " |
| PPm      | " | 29.0/21.9 | 93.3 | 103.3 | 508/35 | 0.17, 0.67 | " |
| CNPm     | " | 28.1/23.4 | 101 | 112.3 | 540/44 | 0.36, 0.62 | " |
| NBO      | ITO/HATCN/TAPC/mCP/EML/TmPyPB/ LIF/Al | 26.1/15.7 | 48.3 | 20.2 | 502/33 | 0.12, 0.62 | [113] |
| NPBP     | " | 28.0/22.8 | 77.6 | 45.4 | 491/29 | 0.09, 0.41 | " |
| BN-TP    | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 35.1/20.8 | 139.3 | 139.3 | 528/36 | 0.26, 0.70 | [114] |
| TW-BN    | ITO/HATCN/TAPC/TCTA/mCP/EML/ TmPyPB/ LIF/Al | 27.8/10.7 | 45.3 | 33.1 | 488/26 | 0.14, 0.36 | [115] |
| TPh-BN   | " | 28.9/15.6 | 54.8 | 43.1 | 492/28 | 0.10, 0.46 | " |
| pCz-BN   | " | 27.2/12.2 | 64.6 | 50.8 | 496/30 | 0.13, 0.54 | " |
| mCz-BN   | " | 25.9/14.0 | 61.2 | 44.7 | 496/31 | 0.15, 0.55 | " |
| BN1      | ITO/HATCN/TAPC/mCP/EML/POT2T/ TmPPyB/ Liq/Al | 24.3/12.9 | 72.8 | 65.3 | 506/36 | 0.15, 0.63 | [116] |
| BN2      | " | 24.5/7.6 | 101.8 | 83.1 | 545/46 | 0.38, 0.61 | " |
| BN3      | " | 24.7/8.9 | 92.6 | 106.4 | 568/43 | 0.47, 0.52 | " |
| BN-ICz-1 | ITO/HATCN/NPB/TCTA/ EML/CzPhPy/ DPPyA/LiF/Al | 30.5/12.8 | – | 84.2 | 523/23 | 0.22, 0.74 | [117] |
| BN-ICz-2 | " | 29.8/22.0 | – | 102 | 523/23 | 0.21, 0.73 | " |
| OAB-ABP-1 | ITO/Plexcore OC AQ-1200/polymer A/ OAB-ABP-1/polymer B/NaF/Al | 21.8/17.4 | 53.2 | 45.3 | 505/33 | 0.12, 0.63 | [64] |
| DMAc-BN  | ITO/PPB/TAPC/mCBP/mCBP/PO9/ B3PyPB/Lif/Al | 20.3/– | – | 503/49 | – | [118] |
| PXZ-BN   | " | 23.3/– | – | 516/47 | 0.22, 0.67 | " |
results bathochromic shift. This is also evident from the DFT studies, where the HOMO orbital of the acceptor substituted MR-core is showed like that of parent core. In contrast, the LUMO orbital was largely delocalized on the acceptor core. As expected, all the compounds showed moderate to large bathochromic-shifted emission compared to the parent core depends on their acceptor unit. The DPTRZ displayed a shoulder emission peak, which negatively impacts color purity. To avoid this, the phenyl or pyrimidine unit was introduced between the parent core and acceptor unit. In the series, the phenyl-substituted derivative (TPTRZ) showed the most redshifted emission with \( \lambda_{PL} \) of 521 nm. Usually, the compounds displayed narrow emission with FWHM \( \leq 35 \) nm. Further, the compounds were applied as dopants in the PhCzBCz host, and the TPTRZ-based device demonstrated superior performance with EQE\(_{\text{max}}\) of 30.6% and CE of 105.8 cd A\(^{-1}\), and green CIE color coordinates of (0.23, 0.68).

Later, Wang et al. extended the \( \pi \)-conjugation of BCz-BN by introducing tert-butylphenyl units on the 3,6-positions of carbazole for developing narrowband green MR-TADF emitter (DtBuPhCzB) and compared its performance with the reference material DtBuCzB.\(^{[76]}\) The DtBuPhCzB exhibited \( \lambda_{PL} \) of 496 nm, which is 16 nm redshifted compared to DtBuCzB, showed \( \lambda_{PL} \approx 481 \) nm in toluene with maintaining narrow FWHM of 21 nm. The DtBuPhCzB revealed small \( \Delta E_{ST} \) of 0.09 eV compared to DtBuCzB (0.13 eV) attributed to its reduced singlet energy caused by the extended conjugation. The PLQY of DtBuPhCzB (97%) was slightly improved compared to

| Compound | Device structure | EQE\(_{\text{max}}\) (1000 cd/m\(^2\)), % | CE, cd/A | \( \text{PE}, \text{lm/W} \) | \( \lambda_{PL}/\text{FWHM} \) [nm] | CIE(x,y) | References |
|----------|------------------|--------------------------------------|-------|----------------|----------------|----------------|-------------|
| TPXZBN   | ITO/HATCN/TAPC/mCP/EML/TmPyPB/LiF/Al | 21.3/17.4 | 64.8 | 37.0 | 506/37 | 0.16, 0.65 | [119] |
| DPXZBN   | " | 19.4/17.2 | 61.6 | 43.2 | 505/36 | 0.15, 0.64 | " |
| BN-DMAC  | ITO/HATCN/TAPC/mCP/mCBP/PO-T2T/TmPyPB/LiF/Al | 21.1/12.5 | 55.2 | 43.4 | 502/48 | 0.14, 0.54 | [72] |
| BN-DPAC  | " | 28.2/19.2 | 77.3 | 56.5 | 504/48 | 0.14, 0.56 | " |
| 2PXZBN   | ITO/HATCN/TAPC/mCP/EML/PO-T2T/TmPyPB/LiF/Al | 17.7/7.4 | 65 | 58 | 522/60 | 0.28, 0.64 | [82] |
| 2PTZBN   | " | 25.5/17.2 | 96 | 86 | 528/58 | 0.28, 0.65 | " |
| SBON     | ITO/HATCN/TAPC/mCP/EML/PO-T2T/TmPyPB/LiF/Al | 13.7/4.3 | 16.1 | 11.4 | 466/28 | 0.13, 0.13 | [120] |
| SBSN     | " | 17.6/12.0 | 40.4 | 25.4 | 492/31 | 0.10, 0.44 | " |
| DBON     | " | 26.7/12.0 | 94.1 | 75.8 | 510/29 | 0.17, 0.68 | " |
| DBSN     | " | 21.8/16.9 | 84.7 | 71.9 | 556/43 | 0.42, 0.57 | " |
| R-BN     | ITO/HATCN/TCTA/CzPhPy/B4PyMMP/LiF/Al | 28.1 | 644/48 | 0.71, 0.28 | [81] |
| R-TBN    | " | 27.6 | 686/49 | 0.72, 0.28 | " |
| BNO1     | TO/HATCN/TAPC/TCTA/mCBP/EML/PO-T2T/ANT-BIZ/LiF/Al | 35.6 | 59 | 66 | 610/39 | 0.64, 0.34 | [121] |
| BNO2     | " | 34.4 | 46 | 52 | 618/39 | 0.65, 0.35 | " |
| BNO3     | " | 36.1 | 43 | 48 | 625/40 | 0.66, 0.34 | " |
| CNC8BNCz | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 33.7/27.1 | -- | 117 | 583/49 | 0.54, 0.46 | [70] |
| (R)-OBN-2CN-BN | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 29.4/21.2 | 67.3 | 70.5 | 496/30 | (0.11,0.52) | [68] |
| (R)-OBN-4CN-BN | ITO/TAPC/TCTA/EML/TmPyPB/LiF/Al | 24.3/2.1 | 70.7 | 74.1 | 508/33 | (0.14,0.64) | " |
| BN4      | ITO/PEDOT-PSS/PVK/EML/DPEPO/TmPyPB/LiF/Al | 20.6/10.7 | 66.30 | 38.58 | 510/49 | (0.18,0.63) | [122] |
| BNSN     | " | 26.5/11.1 | 79.37 | 44.46 | 506/48 | (0.16,0.60) | " |
| (P)-Helicene-BN | ITO/HATCN/TAPC/TCTA/mCP/EML/PO-T2T/ANT-BIZ/Liq/Al | 31.5/18.7 | 117.5 | 153.8 | 523/49 | (0.26,0.66) | [123] |
| (M)-Helicene-BN | " | 30.7/17.9 | 117.8 | 154.2 | 524/50 | (0.26,0.66) | " |
| (S)-BN-MelAc | ITO/HATCN/TAPC/TCTA/mCP/EML/PO-T2T/ANT-BIZ/Liq/Al | 36.1/25.1 | 98.5 | 128.0 | 503/33 | (0.12,0.62) | [124] |
| (R)-BN-MelAc | " | 37.2/26.1 | 103.0 | 130.2 | 504/33 | (0.12,0.63) | " |
DtuBuCzB (91%) because of its improved oscillator strength. The τd of DtuBuPhCzB (61.3 μs) was relatively shorter than the DtuBuCzB (68.9 μs) in 1 wt% doped mCBP film, consistent with the low ΔE_ST. The OLED performance of these compounds was initially tested in mCBP host. The compounds DtuBuCzB and DtuBuPhCzB exhibited bluish-green and green emission with λEL of 488 and 501 nm and FWHM of 29 and 34 nm, respectively. The EQE_max of DtuBuCzB and DtuBuPhCzB is 21.6% and 23.4%, respectively. However, the compounds revealed severe efficiency roll-off at high brightness due to their long τd. Thus, to avoid this, the authors modified the device structure by replacing the mCBP host with the exciplex cohort (TCTA:PIM-TRZ) system and achieved an improved EQE_max of 25.5% in a green color region (0.20, 0.65).

Further, the same group proposed a new design strategy based on frontier molecular engineering, which can couple the advantages of D–A structure and MR-property (Figure 5). They have introduced an auxiliary donor 3,6-di-tert-butyl-carbazole on the HOMO localized meta-carbon of central phenyl ring relative to the B-atom (Bcz-BN). It is expected that the attached carbazole could contribute for the HOMO delocalization and stabilize the respective energy, which results in redshifted emission.[77] As expected, the mCzBNCz showed pure green emission (λPL ~ 519 nm) and a narrow FWHM of 38 nm in solution. Its PL was precisely matched with the solid-state PL, indicating that the aggregation was prevented in the solid-state. In addition, mCzBNCz displayed strong positive solvatochromism in (22 nm), highlighting the merit of design strategy. Further, Yang et al. validated the abovementioned design concept by synthesizing two new MR-TADF emitters, BN-CP1 and BN-CP2. In BN-CP1, the two carbazole donors were substituted at ortho-positions of phenyl linker with respect to the parent MR-TADF core, while in control molecule BN-CP2, the carbazole donor positions were switched on to the meta-position of phenyl linker.[111] Both the compounds showed monomeric photophysical properties in solution and 1 wt% doped film in the mCP host, but in the neat film, they revealed different behavior. In solution and doped film, the compounds showed sky-blue emission with λPL of 490 and 496 nm, respectively. In the case of neat film, the BN-CP2 displayed significant redshift (ΔλPL ~ 521 nm), broad FWHM 48 nm, and reduced PLQY ~ 25% compared to BN-CP1, showing λPL 502 nm, narrow FWHM ~ 26 nm, and high PLQY of 40%. This is attributed to the severe aggregation in BN-CP2, compared to BN-CP1. Nonetheless, both the compounds BN-CP1 and BN-CP2 showed short τd of 79.6 and 83.6 μs and fast k_RISC of 1.56 × 10^7 and 1.43 × 10^7 s^-1, respectively, indicative of their TADF nature. The OLED performance of these emitters was characterized in DMIC-TRZ host. As the doping concentration increases from 1 to 30 wt%, the EL maximum (496 nm) and FWHM (25 nm) were unchanged in BN-CP1, but in the control molecule, BN-CP2 a dramatic redshift with broadened emission was observed, attesting the rationality of the molecular design for suppressing the aggregation-caused emission quenching.
As a result, the HOMO energy of the NBO and NBNP improved with maintaining similar LUMO energy for the materials, which lead to the low bandgap for the compounds and bathochromic-shifted emission. As a result, the compounds NBO and NBNP endowed low $\Delta E_{ST}$ of 0.12 and 0.09 eV, suitable for applying as efficient TADF emitters in OLEDs. Consequently, their $k_{RISC}$ rate was improved to $10^6$ s$^{-1}$ in the doped film compared to the parent compound. This is mainly assigned to their enhanced SOC ($S_1 - T_n$) in NBO of 0.1–0.13 cm$^{-1}$ compared to the parent core of 0.02 cm$^{-1}$. As a result, the compounds exhibited a very high EQE$_{max}$ of 28.0% for NBNP and 26.5% for NBO. Furthermore, due to the high $k_{RISC}$, the compounds showed excellent efficiency stability at high brightness (1000 cd m$^{-2}$) of 25.6% for NBNP and 22.4% for NBO. These results highlight the importance of fusion strategy in shifting the emission wavelengths to the red region with suppressed efficiency roll-off.

Later Wang et al. reported interesting approach by fusing MR core with polycyclic aromatic phenylene unit, BN-TP, featuring para-aligned B and N into the six-membered ring (Figure 6).$^{[114]}$ The photophysical properties revealed that the BN-TP showed a very intense absorption band at 506 nm corresponding to the ICT transition and vivid green emission with a peak wavelength of 523 nm. The observed small Stokes shift $\approx$22 nm and narrow FWHM $\approx$ 34 nm indicates the structural rigidity of BN-TP in the excited state. The calculated $\Delta E_{ST}$, PLQY, and $k_{RISC}$ are of 0.14 eV, 96%, and $2.09 \times 10^4$ s$^{-1}$, indicating the promising TADF characteristic of BN-TP. Then BN-TP applied as a dopant in the PhCzBCz host; it exhibited an EQE$_{max}$ of 35.1%, CE of 139.3 cd A$^{-1}$, and FWHM of 36 nm with green CIE color coordinates of (0.26, 0.70).

Lu and co-workers developed a series of green MR-TADF emitters, TPh-BN, TW-BN, pCz-BN, and mCz-BN, by modifying the parent core with either phenyl or carbazole substituents.$^{[115]}$ As a result of the direct connection of substituents through the single bond, the compounds showed very narrow emission with FWHM of $\approx$20 nm and a small Stokes shift of $\leq$21 nm. All the compounds exhibited high PLQY of $\geq$88% and small $\Delta E_{ST}$ of $\leq$0.15 eV. Indeed, the TPh-BN displayed small $\Delta E_{ST}$, superior PLQY, and a short $\tau_d$ of 0.09 eV, 94%, and 62 $\mu$s. Consequently, TPh-BN exhibited the best performance in the series with EQE of 28.9% and CE of 54.8 cd A$^{-1}$. Notably, it exhibited alleviated efficiency roll-off of 13% at practical brightness without any assistant dopants attributed to its short $\tau_d$. Also, the compounds demonstrated decent operational stability. In the series, TPh-BN displayed the best lifetime with LT$_{50}$ of 36.5 h ($L_0 = 500$ cd m$^{-2}$).

Wang and co-workers reported a new design featuring para-B-$\pi$-B and para-O-$\pi$-O strategy for developing efficient green MR-TADF emitters. It is expected that 1) the two para-disposed B-atoms rather than meta-arrangement in central core could distinctly improve the acceptor strength and lead to the bathochromic shift; 2) the replacement of two para-arylated N-atoms with low atomic energy para-arylated O-atoms can restrict the $\pi$-conjugation of HOMO rather than LUMO to...
hampered the significant redshift with concurrently maintaining MR-feature. Also, the nearly planar conformation and prolonged π-length can endow the high horizontal emitting dipole ratio for better light outcoupling efficiency. To validate the design concept, they synthesized a new MR-TADF emitter named DBNO consisting of five benzene rings clamped by the two para-B atoms and two para-O-atoms in the central phenyl ring. As expected, the DBNO displayed green emission with λPL of 500 nm and extremely narrow FWHM of 19 nm. The OLED fabricated using DBNO as dopant revealed EQEmax of 35.9% and CE of 94.1 cd A−1. Further, its EQE was improved to 37.1% by employing hyperfluorescent device structure, wherein 5T6CBN used as host.

Duan et al. proposed a new design approach featuring the fusion of MR-fragment with the conventional rigid PAHs for developing ultrapure green MR-TADF emitters by suppressing the shoulder peaks.[117] It is expected that, through the precise synthetic fusion of MR-fragment with the conventional PAHs can extend the conjugation length, increase the molecular rigidity, and reduce the vibrational relaxations in excited state. To rationalize the design concept, they developed two new MR-TADF emitters BN-ICz-1 and BN-ICz-2, by fusing MR fragment with the indolocarbazole-type rigid core.[117] DFT studies revealed that the BN-ICz core exhibited much improved oscillator strength and narrowed optical bandgap than the conventional rigid PAHs attributed to its extended conjugation length. The shoulder peak intensity of BN-ICz’s was reduced compared to the ICz core validates the benefit of design strategy. Nonetheless, the BN-ICz-1 and BN-ICz-2 exhibited green emission with λPL of 521 nm and FWHM of 21 nm, which is significantly reduced compared to the ICz’s (34 nm). Further, the potential of these materials as green dopants in OLEDs was tested in sensitized device system. The BN-ICz-1 and BN-ICz-2 showed EQEmax of 30.5% and 29.8% in pure green region with λPL of 506 nm and FWHM of 34 nm. The improved SR-CT delocalization and fully fused molecular electron-rich O-atom. Both the compounds DBNO consisting of five benzene rings clamped by the two para-B atoms and two para-O-atoms in the central phenyl ring. As expected, the DBNO displayed green emission with λPL of 500 nm and extremely narrow FWHM of 19 nm. The OLED fabricated using DBNO as dopant revealed EQEmax of 35.9% and CE of 94.1 cd A−1. Further, its EQE was improved to 37.1% by employing hyperfluorescent device structure, wherein 5T6CBN used as host.

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Later, Yang et al. modified the DMAC-BN by replacing two methyl units in acridine with phenyl units resulted a new green MR-TADF emitter, BN-DPAC, and compared its properties with the reference material BN-DMAC.[72] As expected, the emission of BN-DMAC and BN-DPAC redshifted compared to DABNA-1 attributed to its strengthened SR-CT. The compounds BN-DMAC and BN-DPAC acquired low ΔEST of 0.14 and 0.11 eV and short τD of 13.9 and 11.6 μs, respectively, compared to the reference DABNA-1. Notably, the BN-DPAC displayed significantly improved kRISC of 1.26 × 105 s−1. The OLEDs of the compounds showed pure green emission with λEL of 502 and 504 nm, respectively. The BN-DPAC exhibited EQEmax of 22.8% attributed to its high kRISC. Further, the EQEmax of BN-DPAC was promoted to 30% employing TADF-type exciplex host system. Furthermore, same group developed new design to promote the RISC of MR-TADF emitters by introducing heavy atom (S) into the MR-framework. To validate the proof-of-concept, they synthesized phenothiazine containing MR-core (2PTZBN) and compared its properties with the phenoxazine derivative (2PXZBN).[82] DFT and PL studies revealed that the incorporation of S in 2PTZBN benefited to reduce the ΔEST and improve the SOC, which resulted high kRISC of 2.8 × 105 s−1 compared to the reference compound 2PXZBN. Consequently, the 2PTZBN-based OLED exhibited excellent EQEmax of 25.5% and suppressed efficiency roll-off by maintaining its high EQE of 17.2% at 1000 cd m−2. These results indicate that the heavy atom doping into the MR-TADF emitters is advantageous for accelerating the kRISC without compromising the MR-effect.

The chiral thermally activated delayed fluorescence (TADF) emitters possessing circularly polarized electroluminescence (CPEL) attracted increasing attention due to their promising...
Despite the abundance of CPL active conventional TADF emitters, miniscule examples of CPL active MR-TADF emitters have been documented. For example, Wang et al. reported two CPL-active MR-TADF emitters, (R/S)-OBN-2CN-BN and (R/S)-OBN-4CN-BN. They used a chiral perturbation strategy by grafting chiral (R/S)-octahydrobinaphthol (R/S)-OBN units onto an MR-TADF molecule. As a result, both emitters exhibited green emission with an FWHM of ≤27 nm. Furthermore, these emitters manifested a small ΔE_{ST} of ≤0.13 eV. Further, the CPL spectra of two pairs of chiral enantiomers (3 wt% doping concentration) in PhCzBCz-doped films show almost mirror-image relationships with photoluminescence dissymmetry factors (g_{PL}) of +1.43 × 10^{-3}/-1.27 × 10^{-3} and +4.60 × 10^{-4}/-4.76 × 10^{-4}, respectively.

Further, to improve the glum value, Chou et al. developed asymmetrical MR-TADF enantiomers, (P,P',P')/(M,M',M')-BN4 and (P,P',P')/(M,M',M')-BN5. These materials exhibited narrowband green emission with FWHM of 43 nm (BN4) and 44 nm (BN5). Due to the incorporation of a heavy atom (S), the material BN4 showed a high k_{RISC} of 1.6 × 10^{5} s^{-1}, while BN5 revealed k_{RISC} (0.76 × 10^{5} s^{-1}). The compounds exhibited prominent circular dichroism (CD). However, due to the cotton applications in 3D displays. Despite the abundance of CPL active conventional TADF emitters, miniscule examples of CPL active MR-TADF emitters have been documented. For example, Wang et al. reported two CPL-active MR-TADF emitters, (R/S)-OBN-2CN-BN and (R/S)-OBN-4CN-BN. They used a chiral perturbation strategy by grafting chiral (R/S)-octahydrobinaphthol (R/S)-OBN units onto an MR-TADF molecule. As a result, both emitters exhibited green emission with an FWHM of ≤27 nm. Furthermore, these emitters manifested a small ΔE_{ST} of ≤0.13 eV. Further, the CPL spectra of two pairs of chiral enantiomers (3 wt% doping concentration) in PhCzBCz-doped films show almost mirror-image relationships with photoluminescence dissymmetry factors (g_{PL}) of +1.43 × 10^{-3}/-1.27 × 10^{-3} and +4.60 × 10^{-4}/-4.76 × 10^{-4}, respectively.

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effect, the chiral analogues BN4 and BN5 displayed notable changes in the spectral shapes of CPL signals, with PL dissymmetry factors ($|g_{PL}|$) of $(1.0–2.0) \times 10^{-3}$. Further, when doped in mCPCN film, the cotton effect was strongly exhibited, which resulted in mirror image CPL spectra with ($|g_{PL}|$) of $+1.1 \times 10^{-3}/-1.0 \times 10^{-3}$ and $+1.3 \times 10^{-3}/-1.0 \times 10^{-3}$, respectively. These values are higher than that of the (R/S)-OBN-based MR-TADF via indirect chiral perturbation strategy. Further, the solution processed OLEDs, manifested intense green emissions. The devices achieved high EQE max of 20.6% and 22.0% for BN4 and BN5, respectively. Notably, the enantiomers of BN4-based devices clearly displayed mirror-imaged CPEL signals with $g_{EL}$ of $+3.7 \times 10^{-3}/-3.1 \times 10^{-3}$, while the corresponding BN5-based devices showed CPEL with $g_{EL}$ of $+1.9 \times 10^{-3}/-1.6 \times 10^{-3}$.

Yang et al. reported a pair of helicene-based enantiomers, namely, (P)-helicene-BN and (M)-helicene-BN.[123] The design is based on merging the helical chirality with B/N/S-inserted PAH skeleton. The designed emitter exhibited narrowband green emission with an FWHM of 46 nm. Further, the $g_{PL}$ were measured in toluene, which are $+2.0 \times 10^{-3}$ for (P)-helicene-BN and $-2.1 \times 10^{-3}$ for (M)-helicene-BN. In doped films, the $g_{PL}$ values are $+1.3 \times 10^{-3}$ for (P)-helicene-BN and $-2.0 \times 10^{-3}$ for (M)-helicene-BN, indicating that no racemization occurred during the thermal deposition process. The OLED exhibited

![Chart 6. Chemical structures of the orange/red MR-TADF emitters.](image)

![Figure 7. Design approach for developing red MR-TADF emitters.](image)
green emission with FWHM of ≤ 50 nm. Due to similar photophysical properties of both (P)-helicene-BN and (M)-helicene-BN, both devices manifested identical performances. The devices exhibited EQEmax over 30% with relatively low roll-off characteristics. Further, both helicenes exhibited mirror image CPEL with a $|g_{EL}|$ value of $2.2 \times 10^{-3}$ for (M)-helicene-BN and $+1.2 \times 10^{-3}$ for (P)-helicene-BN, respectively.

Later, to obtain a small FWHM in CPL active MR-TADF compounds, some group developed two new chiral emitters, namely, (R)-BN-MeIAc and (S)-BN-MeIAc.[124] These emitters manifested not only small FWHM (30 nm), but the low $\Delta E_{ST}$ of 0.11 eV. Furthermore, these materials exhibited good morphological stability with decomposition temperature of 430 °C. The $g_{EL}$ were measured and are of $+2.5 \times 10^{-4}$ and $-2.5 \times 10^{-4}$ for (R)-BN-MeIAc and (S)-BN-MeIAc, respectively. The CP-OLEDs demonstrated impressive EQEmax of 37.2% and 36.1%, PE of 130.2 and 128.0 lm W⁻¹ for (R)-BN-MeIAc and (S)-BN-MeIAc, respectively. These are the highest efficiencies among the reported B-based CP-TADF emitters. Such high EQE values are supported by the high horizontal emitting dipole ratio ($\Theta//\theta$) of 90%. Importantly, the devices displayed distinct CPEL signals with $g_{EL}$ of $+2.7 \times 10^{-4}$ for (R)-BN-MeIAc and $-2.9 \times 10^{-4}$ for (S)-BN-MeIAc.

### 4. Orange/Red MR-TADF Emitters

As discussed above, the development of pure red emitters is highly demanding for the fabrication of full-color OLEDs and imaging applications.[10,21,130,131] Despite of the great potential of MR-TADF emitters in blue and green regions, the narrowband red emitters are scarcely reported because of their intrinsic trade-off between the bathochromic-shifted emission and color purity.[112–135] For example, inspired by Yasuda et al. (vide infra), Duan et al. developed multiple B- and N-embedded polycyclic heteroaromatic motifs by arranging B and N atoms in the form of para-B-$\pi$-B and para-N-$\pi$-N on central phenyl ring (R-BN and R-TBN) (Chart 6).[81] As a result of significantly enhanced donor and acceptor strengths of N and B, the HOMO and LUMO energies are well stabilized and lead to the very narrow bandgap $\leq$ 1.7 eV. Consequently, the R-BN and R-TBN showed deep-red emission with $\lambda_{PL}$ of 662 and 692 nm, respectively, without compromising their MR-effect. Notably, both the materials displayed unity PLQY and very short $\tau_d$ and high $k_{RISC} \approx 10^4$ s⁻¹. These results highlight the superiority of para-B-$\pi$-B and para-N-$\pi$-N approach for constructing deep-red MR-TADF emitters. Further, the performance of these materials in OLEDs was tested in ternary system using Ir(mphq)₂tmtd as sensitizer and exhibited deep-red emission with $\lambda_{EL}$ of 664 and 686 nm and FWHM of 48 and 49 nm, respectively. As a result, they exhibited deep-red color coordinates of (0.71, 0.28) and (0.72, 0.27), respectively. Unprecedently, the EQEmax of the R-BN and R-TBN was demonstrated to be 28.1% and 27.6%, respectively. It is also noteworthy to mention that the devices displayed exceptional operational stability with LT90 of 125 and 151 h at $I_0$ of 2000 cd m⁻².

Inspired by this report, Yang et al. constructed a series of pure red-MR TADF emitters by replacing the two N-atoms with arylated O-atoms by para-positioning O-$\pi$-O and N-$\pi$-N and B-$\pi$-B (BNO1-BNO3).[112] The emission wavelengths of the materials are fine-tuned by peripheral decoration of aryl units on O-atom (Figure 7). In the series, BNO3 exhibited pure-red emission with $\lambda_{PL}$ of 616 nm and FWHM of 33 nm. Photophysical studies revealed marked PLQY ≥ 95% and narrow $\Delta E_{ST}$ and short $\tau_d$, indicating their ability to exhibit TADF property. Further, they fabricated phosphor sensitized OLED and BNO3 outperformed with EQEmax of 36.1% and it maintained very high EQE of 28.6% at 10 000 cd m⁻². Importantly, all the materials exhibited pure-red emission with CIE(x,y) of 0.64–0.67. Further, BNO1 showed decent operational stability with LT90 of 49.8 h.

In 2021, Bin et al. reported a new molecular design by introducing CN acceptor and carbazole donors on LUMO and HOMO located carbons of the central phenyl unit in the MR-skeleton (CNCz-BNCz) (Chart 6). As expected, the emission wavelength of CNCz-BNCz realized in orange-red region ($\lambda_{PL} \approx$ 583 nm). Notably, benefited by the simple molecular structure of CN, the FWHM of the CNCz-BNCz was unchanged compared to the reference material due to the suppressed structural relaxations in the excited state. The photophysical properties indicating that the CNCz-BNCz possesses prominent MR-TADF effect with the aid of its small $\Delta E_{ST}$ of 0.18 eV and high $k_{RISC}$ of $4.2 \times 10^4$ s⁻¹. The optimized OLED of CNCz-BNCz in TADF sensitized system demonstrated EQEmax of 33.7% and pure orange-red emission ($\lambda_{PL} \approx$ 584 nm), CIE(x,y) of (0.54, 0.46). These results indicate that the attachment of simple CN acceptor at para-carbon relative to B-atom is advantageous for shifting toward red region without compromising color fidelity.

![Figure 8](https://www.advancedsciencenews.com)  
Figure 8. Design tactics for tuning the emission of narrowband MR-TADF emitters from blue to red.
5. Full-Color MR-TADF Emitters

It is imperative to develop a feasible molecular design for tuning the emission colors of MR-TADF emitters from deep-blue to red region for full-color display applications (Figure 8). In 2021, Yasuda et al. reported an epoch-making strategy for producing the full-color and narrowband MR-TADF emitters by the judicious choice of B and carbazole units. They chose BBCz-SB (2) as a parent core. The introduction of B-atom on para-carbon of central core relative to the N-atom reduces the donating strength of N-atom. Similarly, the addition of N-atom para- to the B-atom reduces the acceptor strength of B-atom; thus, the compound BBCz-DB displayed large band gap and blue-shifted emission. Besides, in BBCz-R (5), the N- and B- were substituted para- to each other in a fused PAH framework, leading to the reduced band gap and red-shifted emission compared to the parent core. The design strategy was validated with the aid of computational studies. Employing this strategy, it is possible to fine-tune the emission colors of MR-TADF emitters from deep-blue to the deep-red region in B/N-featured PAHs. Further, they synthesized two D–A-type MR-TADF emitters by integrating the core structure 2 with either three or two carbazole units, yielding BBCz-G (3) and BBCz-Y (4), respectively. The compounds 1-5 displayed tunable emission colors from deep-blue to deep-red with wavelengths of 446, 489, 517, 549, and 615 nm, respectively. In the series, 1 and 5 exhibited narrow FWHMs of 16 and 21 nm, respectively, due to their fully fused molecular structures. All the compounds revealed high PLQY and low $\Delta E_{ST}$ and a high $k_{RISC}$ suitable to apply as dopants in OLED. When these materials were used as dopants (2 wt%) in the mCBP host, similar to the PL...

Chart 7. Design of full-color MR-TADF emitters.
emission, the compounds showed tunable emission colors from deep-blue to deep-red. Notably, the CIE color coordinates of compounds 1, 3, and 5 matched with the three primary colors, blue (0.12, 0.18), green (0.26, 0.68), and red (0.67, 0.3), respectively. Nonetheless, compounds 1-5 displayed high EQE$^{\text{max}}$ of 29.3%, 27.8%, 31.8%, 29.3%, and 22.0%, respectively, attributed to their high PLQY and tendency to spontaneously adopt horizontal emitting dipole orientation in the film.

Later, the same group proposed a straightforward design for constructing color-tunable MR-TADF emitters by modifying the parent core. CzB, either with electron-withdrawing imine or electron-donating amine units ([Cz-B-DACzB]$^{[71]}$ The emission wavelengths of the compounds were tuned from blue (460 nm) to yellow (576 nm) depending on the donor strength of the appended chromophores. In the series, the imine containing derivative Cz-B exhibited deep-blue emission because of electron-withdrawing imine N-atom in the HOMO-distributed carbon, which depressed the HOMO energy and increased the bandgap. However, the carbazole or diphenylamine substituted derivatives displayed more redshifted emission because of the stabilized HOMO energy and reduced bandgap. Indeed, the diphenylamine featured derivative exhibited redshifted emission in the series compared to the carbazole due to its strong donor strength. All the compounds displayed narrow emission with FWHM $\leq$ 35 nm and low $\Delta$E$_{ST}$. Their OLED performance was investigated either in oCBP or mCBP hosts. In the series, the carbazole-substituted derivative exhibited the best performance with EQE$^{\text{max}}$ of 29.2% and CE of 100.7 cd A$^{-1}$.

Further, Yang et al. reported peripheral decoration strategy of MR-fragment with the strong electron donors. They modified the well-known CzB core with carbazole (BN1), monodiphenylamine (BN2), and di-diphenylamine (BN3) units.$^{[116]}$ The emission wavelengths of the compounds tuned from blue ($\lambda_{PL} \approx 496$ nm) to yellow ($\lambda_{PL} \approx 562$ nm) depending on the donor strength and number of appended chromophores. In the series, the BN3 exhibited yellow emission and low $\Delta$E$_{ST}$. These results attest the superiority of peripheral decoration strategy for color tuning the MR-TADF emitters without effecting on the MR-property. When applied these materials as dopant emitters in OLED, the BN3 outperformed with maximum EQE of 24.7% and CE of 92.6 cd A$^{-1}$ in the yellow region with CIE color coordinates of (0.47, 0.52).

Recently, Zheng et al. reported four ternary B/N-based MR-TADF emitters (SBON, SBSN, DBON, and DBSN) employing B-π-C and E-π-E strategy (E = O or S) for tuning the emission wavelengths from blue ($\lambda_{PL} \approx 463$ nm) to yellow ($\lambda_{PL} \approx 553$ nm) region.$^{[120]}$ The coordination between the B/N and S/O atoms played a vital role in regulating the CT delocalization and emission colors. This approach endowed narrow band emission for all the compounds with FWHM $\leq$ 28 nm. The diboron embedded derivatives DBON and DBSN showed high PLQY of 98% is attributed to its extended π-conjugation and suppressed nonradiative deactivations. The S-containing materials SBSN and DBSN revealed high $k_{\text{RISC}}$ of 1.5 $\times$ 10$^7$ and 1.9 $\times$ 10$^5$ s$^{-1}$, compared to the O-derivatives, SBON and DBON, because of the strong SOC with the aid of heavy-atom effect of S atom. The OLED fabricated with DBON demonstrated best performance in the series with EQE$^{\text{max}}$ of 26.7% and (CIE $x$;$y$) $\approx$ 0.17, 0.68 (Chart 7).

6. Conclusion and Outlook

B-based MR-TADF emitters fascinated the researchers with their unprecedented color purity (FWHM $<$ 40 nm) and excellent EQE $>$ 35%. As a result, numerous MR-TADF materials have been derived to expand their structural diversity and understanding the emission mechanism. Although the MR-TADF emitters have potentially overcome the major obstacles of state-of-the-art D–A-type TADF emitters, they are suffering from low $k_{\text{RISC}}$, severe efficiency roll-off, poor operational stability, and aggregation-caused emission quenching and difficult to realize ultrawide color gamut emitters. In this review, we have summarized the different design strategies reported till date to mitigate the aforementioned shortcomings of MR-TADF emitters (Figure 9).

First, the production of ultrawide colour gamut MR-materials is essential for the fabrication of full-color high-definition OLED displays. However, the fused molecular framework with enefbled ICT characteristic restricts the emission in blue region (470–500 nm). To shift the emission into deep-blue region ($< 460$ nm), the incorporation of electron-deficient imine N or the replacement of amine N with O/S was reported to be an ideal strategy. It is also reported that the meta-B-π-B and E-π-E (E = N/O/S) arrangement could interrupt the effective CT delocalization and increase the bandgap of emitters. The peripheral modification of MR-skeleton with either D or A units judiciously tunes the emission beyond blue region. For example, substitution of D and A units on HOMO- and LUMO-dominated carbons of MR-core can stabilize respective energies, and reduce the bandgap, which leads to the redshifted emission. The emission wavelength can be toggled between green and yellow by managing the strength of appended donor or acceptor units. Also, the integration of MR-core with the rigid PAHs is another promising strategy to construct the narrowband green emitters.

![Figure 9](image-url)
The red MR-TADF emitters associated with narrow FWHM are scarcely reported due to their limited scope for molecular design and structural diversity. Till date only one design has been reported for devising red MR-TADF emitters, i.e., para-B-π-B and N-π-N arrangement with the extended fused π-skeleton. Nonetheless, it is highly desirable to develop the new molecular designs for red MR-TADF emitters. The linearly extended MR-TADF emitters can improve the CT delocalization and reduce the ΔE_{CT} and τ_{4}. Most of the reported MR-TADF emitters exhibit inferior k_{RISC} in the order of ∼10^{3} s^{-1}, which is detrimental for stability and efficiency roll-off. Construction of emitters with heavy atoms such as S and Se is important for high k_{RISC} and low τ_{4} because of their strong SOC. The linearly extended molecular geometries with multiple B-atoms can benefit high k_{RISC}. Also, PAH-integrated MR-TADF emitters realized high k_{RISC} because of their low ΔE_{CT}. The FWHM of the emitters can be narrowed by fully fused molecular conformation and multiple B encapsulation in the molecular framework. The aggregation-caused emission quenching is one of the critical parameters in MR-TADF emitters attributed to their planar geometries. The employment of nonplanar molecular conformation and protection of MR-core with shielding groups can restrain the formation of aggregation. Further, efficiency roll-off at high brightness can be alleviated by the high k_{RISC} and short τ_{4} of the emitters. Finally, the operational lifetime is one of the most important parameters of MR-TADF emitters. So far, no ubiquitous design has been reported in material design perspective; however, construction of MR-core with rigid PAHs together with high BDE of B-C bond could improve the chemical stability of the emitters. The high k_{RISC} and short τ_{4} are vital to suppress the triplet exciton accumulation, which reduces the undesirable TTA or TPQ. Besides, employment of MR-emitters as terminal dopant in hyperfluorescent devices is proficient approach for improving the operational lifetime. Recently, Lee et al. proposed a tandem device engineering strategy to promote the operational lifetime of MR-TADF emitters. This result would expiate the new device engineering approaches for improving the operational stability of MR-OLEDs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

full-color, multiresonance, organic light-emitting diodes, stability, thermally activated delayed fluorescence

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