Multiresonant Thermally Activated Delayed Fluorescence Emitters Based on Heteroatom-Doped Nanographenes: Recent Advances and Prospects for Organic Light-Emitting Diodes

Subeesh Madayanad Suresh, David Hall, David Beljonne, Yoann Olivier, and Eli Zysman-Colman*

Since the first report in 2015, multiresonant thermally activated delayed fluorescent (MR-TADF) compounds, a subclass of TADF emitters based on a heteroatom-doped nanographene material, have come to the fore as attractive hosts as well as emitters for organic light-emitting diodes (OLEDs). MR-TADF compounds typically show very narrow-band emission, high photoluminescence quantum yields, and small \( \Delta E_{ST} \) values, typically around 200 meV, coupled with high chemical and thermal stabilities. These materials properties have translated into some of the best reported deep-blue TADF OLEDs. Here, a detailed review of MR-TADF compounds and their derivatives reported so far is presented. This review comprehensively documents all MR-TADF compounds, with a focus on the synthesis, optoelectronic behavior, and OLED performance. In addition, computational approaches are surveyed to accurately model the excited state properties of these compounds.

1. Introduction

Delayed fluorescence (DF) was first identified by Francis Perin (1929),[3] in uranyl salts. DF was later studied in detail by Magel and co-workers[2] (1941) in fluorescein followed by studies in other \( \pi \)-conjugated compounds such as eosin,[3] fullerene,[4] benzophenone,[5] aromatic thiiones,[6] thietones,[7] and 9,10-anthraquinone.[8] For many years, molecules for thermally activated delayed fluorescence (TADF), also known as E-type fluorescence for eosin Y, were not given much attention due to the lack of potential applications and the generally low measured photoluminescence quantum yields. In 2009, Adachi and co-workers reported a Sn(IV) porphyrin as a TADF emitter and employed it in OLEDs.[9] In the following year, Deaton et al. reported a dinuclear copper(I) complexes showing TADF.[10] These initial reports catalyzed a resurgence of interest in the molecular design of copper(I) complexes as emitters for OLEDs by the likes of Yersin and co-workers,[11] Thompson and co-workers,[12] Bräse and co-workers,[13] among many others.[14] The first purely organic TADF emitter used in an OLED was reported by Adachi and co-workers in 2011.[15] The EQE of the OLED was only 5.3%, and thus failed to provide convincing evidence that TADF is activated in the exciton-harvesting process. In 2012, the same group introduced a series of highly efficient organic TADF emitters composed of carbazole electron donating (D) and phthalonitrile accepting (A) units.[16] The resultant structures present a large twisting angle between the D and A units that reduces overlap between the frontier HOMO and LUMO molecular orbitals, and as a result produces a small singlet–triplet energy gap (\( \Delta E_{ST} \)). The best performing OLED, using the now well-known 4CzIPN, showed an EQE\(_{\text{max}}\) of 19.3%. This seminal contribution triggered huge research efforts to develop TADF materials for a number of applications[17] aside from electroluminescent devices: these include oxygen sensing,[18] photocatalysis,[19] electrochemiluminescence,[20] lasers,[21] and bioimaging.[22] According to spin statistics, hole and electron recombination upon electrical excitation of the emitter results in a 3:1 ratio of triplet excited states with respect to singlets.[23] In TADF systems, the lowest excited singlet (S\(_1\)) and triplet (T\(_1\)) states are very close in energy to each other. The small \( \Delta E_{ST} \), typically less than 200 meV, provides an avenue for thermal upconversion of previously nonemissive triplet
excitons into emissive singlet excitons via reverse intersystem crossing (rISC).\cite{17} According to El-Sayed’s rule, the two excited states must originate from different orbitals in order to facilitate the required spin–orbit coupling mediating rISC.\cite{24} Via TADF, 100% internal quantum efficiency (IQE) can be realized in EL devices, the result of the harvesting of 100% of the excitons. To achieve high-performance TADF emitters, fast rISC rates are required, which are governed by a combination of small $\Delta E_{ST}$ and large spin–orbit coupling (SOC), the latter mediated in part by the presence of heavy atoms in the emitter. Samantha et al. identified that the strength of the SOC in D–A organic molecules relies mainly on difference in the nature of the $S_1$ and $T_1$ excited states.\cite{25} However, the emitter must also possess high photoluminescence quantum yield, $\Phi_{PL}$, which is a function of the oscillator strength of the radiative transition from the $S_1$ state. As a consequence of the D–A molecular design, the lowest singlet and triplet excited states bear a strong intramolecular charge transfer (ICT) character that is linked with a small $\Delta E_{ST}$. However, the small $\Delta E_{ST}$ usually is associated with a small oscillator strength of the $S_1$-$S_0$ transition as both parameters are essentially proportional to the overlap between the hole and electron densities. It is thus extremely difficult to obtain TADF emitters that at once possess both small $\Delta E_{ST}$ and large $\Phi_{PL}$. Another weakness in D–A TADF emitter design is the broad emission band originated from the ICT-emissive singlet state. The broadness both results in poorer color purity and also is emblematic of increased vibrational motion, which can lead to increased nonradiative decay rates.\cite{27}

2. Multiresonant-TADF Emitter Design

Recently, Hatakeyama and co-workers\cite{28} introduced a potential solution, coined multiresonance TADF (MR-TADF), by designing planar boron- and oxygen (or nitrogen)-containing arene compounds. MR-TADF compounds are a new class of fused polyyclic aromatic compounds having electron donating atom (donor) and electron deficient atom (acceptor) disposed para to each other in a fused planar polyyclic aromatic framework.\cite{27a,28,29} Due to their complementary resonance effects the electron density distributions on the HOMO and LUMO orbitals are offset by one atom as illustrated in Figure 1. In MR-TADF compounds the electron-rich regions are mainly on the donor atoms and carbon atoms positioned ortho and para to them while the electron-deficient regions are localized on the acceptor atoms and the carbon atoms positioned ortho and para to them. In the lowest singlet and triplet excited states, the electron density distribution is delocalized over the entire arene but with alternative electron-rich and electron-poor regions while the electron-density distribution shows the same alternating pattern in the ground state, yet with electron-rich and electron-poor regions being switched. The resulting transition from $S_1$ to $S_0$ therefore features a short-range reorganization of the electron density while, importantly, maintaining a high degree of electron–hole overlap. In MR-TADF, the Franck–Condon excitations show high oscillator strength, reminiscent of locally excited (LE) states, leading to both efficient delayed fluorescence and high $\Phi_{PL}$. Thus, MR-TADF molecules combine in a rather unique fashion long-range interactions and delocalization effects the electron density distributions on the HOMO and LUMO orbitals. It is thus very difficult to obtain TADF emitters that at once possess both small $\Delta E_{ST}$ and large $\Phi_{PL}$. Another weakness in D–A TADF emitter design is the broad emission band originated from the ICT-emissive singlet state. The broadness both results in poorer color purity and also is emblematic of increased vibrational motion, which can lead to increased nonradiative decay rates.\cite{27}

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Suresh obtained his M.Sc. in analytical chemistry from Maharajas College Ernakulam. He then moved to Pusan National University in 2013 for a Ph.D. under the supervision of Prof. Youngson Choe. During this period, his research focused on developing small organic molecules for light-emitting electrochemical cells (LEECs). He then moved to the University of St Andrews for a postdoctoral fellowship with Prof. Eli Zysman-Colman working on the design of thermally activated delayed fluorescent (TADF) emitters for organic light-emitting diodes (OLEDs). In 2019, he received the Marie Skłodowska-Curie Individual Fellowship with Prof. Eli Zysman-Colman for developing MR-TADF emitters for OLEDs and LEECs.

David Hall obtained his MChem from the University of Durham working with Prof. Martin Bryce where he worked on the synthesis of donor–acceptor systems directed toward thermally activated delayed fluorescence (TADF) or room temperature phosphorescence (RTP). Currently, he is a cotutelle student between the University of St Andrews and the University of Mons under the guidance of Prof. Eli Zysman-Colman and Prof. Yoann Olivier, respectively. His research focuses on computational design, synthesis and optoelectronic characterization of novel TADF emitters, primarily multiresonant-TADF compounds.

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obtained his Ph.D. from McGill University in 2003 with Prof. David N. Harpp as an FCAR scholar. He then completed two postdoctoral fellowships, one at Jay Siegel at the University of Zurich as an FQRNT fellow and the other with Stefan Bernhard at Princeton University as a PCCM fellow. He started his independent career in Canada in 2007. In 2013, he moved to the University of St Andrews where he is presently Professor of Optoelectronic Materials and Fellow of the Royal Society of Chemistry. His research program focuses on emitter design for electroluminescent devices and photocatalyst development.
effects prompting high radiative decay rates with short-range charge density reshuffling minimizing the singlet–triplet gap. Further, the rigid nature of the emitter results in significantly reduced vibrational motion that is reflected in a much narrower emission band.

In 2015, Hatakeyama and co-workers reported a one-step borylation method to synthesize a series of high band gap B,O-doped polycyclic aromatic molecules with a 1,4-oxaborine substructure.[28] The core structure consists of two donor oxygen atoms and one boron acceptor positioned para to both oxygen atoms. The core structure was generated by ortho lithiation followed by trans-metalation and tandem electrophilic arene borylation of 1,3-diaryloxybenzene and its derivatives. Using these reaction conditions, they synthesized a series of B,O-doped compounds sharing the same 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracence in moderate to good yields (42–74%). The versatility of this one-step borylation is demonstrated by rather diverse examples, including phenyl and phenoxy derivatives of B,O core and a boron-fused benzo[6]helicence[28] (Figure 2). The electron-rich oxygen atoms accelerate the borylation rate by enhancing the nucleophilicity of the arene. The photophysical properties of the emitters are summarized in Table 1. The parent molecule 2a exhibited near UV emission with a λ<sub>PL</sub> of 398 nm and high Φ<sub>PL</sub> of 72% in dichloromethane. The phosphorescence spectrum at 77 K in EtOH glass was observed at 418 nm, which translates to a very high triplet energy level of 2.97 eV. The corresponding ΔE<sub>ST</sub> for 2a is small at 0.15 eV, which is comparable to that of a conventional donor–acceptor TADF compounds.[17] Modifying the parent compound with phenyl units (2b–d) redshifted the emission maxima to different extents based on the position of phenyl substituents. The most redshifted emission in the series was observed for 2d, where the both phenyl units are mesomerically conjugated to both oxygen donor atoms; interestingly, no change in the fluorescence maximum, λ<sub>PL</sub>, was observed when the position of phenyl rings is changed.

Figure 1. Schematic representation of energy levels and HOMO and LUMO distribution of MR-TADF molecule, where E<sub>VA</sub> is vertical absorption, E<sub>VF</sub> is vertical fluorescence, and E<sub>A</sub> is adiabatic energy.

Figure 2. Chemical structures, photophysical properties, and device performances of 2a-c and 4. Adapted with permission.[28] Copyright 2015, Wiley-VCH.
Table 1. Physical properties of previously reported MR-TADF and those with an MR-TADF acceptor compounds.

| Compound | λ_{vis} | FWHM | Φ_{PL} | S1 | T1 | ΔE_{ST} | τ_{PL} | k_{RISC} | Ref. |
|----------|---------|-------|--------|----|----|--------|-------|---------|------|
| 2a       | 398      | 34    | -72    | 3.12 | 2.97 | 0.15   | -     | -       | [28] |
| 2b       | 410      | 28    | -65    | 3.02 | 2.81 | 0.21   | -     | -       |       |
| 2c       | 410      | 33    | -60    | 3.02 | 2.71 | 0.31   | -     | -       | [28] |
| 2d       | 436      | 49    | -57    | 2.84 | 2.70 | 0.14   | -     | -       | [28] |
| 2e       | -492     | -96   | -92    | 2.52 | 2.46 | 0.06   | -     | -       | [28] |
| DABNA-1  | 462      | 33/30 | 89/88  | 2.67 | 2.49 | 0.18   | 93.7  | 9.9     | [27a] |
| DABNA-2  | 470      | 34/28 | 85/90  | 2.61 | 2.47 | 0.14   | 65.3  | 14.8    | [27a] |
| 2a       | 403      | -26   | 36/54  | 3.11 | 2.90 | 0.21   | -     | -       | [33] |
| 1        | 386      | 48/43 | 63/73  | -   | -   | -      | -     | -       |       |
| B2       | 461      | 39/32 | 39/53  | 2.73 | 2.54 | 0.19   | -     | -       | [29a] |
| B3       | 442      | 50/34 | 13/34  | 2.81 | 2.66 | 0.15   | -     | -       | [29a] |
| B4       | 449      | 22/38 | 21/57  | 2.76 | 2.61 | 0.15   | -     | -       | [29a] |
| B2-F     | -467     | -44   | -57    | 2.66 | 2.51 | 0.15   | -     | -       | [29a] |
| TBN-TPA  | 470      | 26    | 97     | -   | -   | 0.014  | 51.0  | -       | [36] |
| t-DABNA  | 445      | -     | -85    | 2.80 | 2.63 | 0.17   | 83.3  | 2.4     | [38] |
| υ-DABNA  | 468      | 14/18 | 74/90  | 2.64 | 2.62 | 0.017  | 4.1   | 2.0     | [29b] |
| DOBNA-OAr| 388      | 34/18 | 65/73  | -   | -   | -      | -     | -       | [29b] |
| Tc2-BN   | 477      | 22/55 | -      | -   | -   | -      | -     | -       | [48] |
| 2F-BN    | 494      | 26/32 | 95/89  | 2.53 | 2.35 | 0.16   | 25.9  | 2.4     | [48] |
| 3F-BN    | 499      | 27/33 | 90/83  | 2.48 | 2.40 | 0.08   | 16.7  | 3.9     | [48] |
| 4F-BN    | 496      | 26/31 | 99/91  | 2.50 | 2.39 | 0.11   | 19.0  | 4.4     | [48] |
| α-3BNOH  | 390      | 31/32 | 50     | 3.12 | 2.81 | 0.31   | 0.45  | -       | [50] |
| ADBNA-Me-Mes  | -482     | -33   | -89    | 2.57 | 2.39 | 0.18   | 165.6 | 7.6     | [54] |
| ADBNA-Me-Tip  | -479     | -34   | -88    | 2.59 | 2.41 | 0.18   | 147.0 | 9.0     | [54] |
| 3        | 482      | 71/84 | 2.56   | 2.38 | 0.18  | -      |       |         |       |
| 4a       | 485      | 88/91 | 2.54   | 2.35 | 0.19  | -      |       |         |       |
| 4b       | 487      | 85/93 | 2.53   | 2.34 | 0.19  | -      |       |         |       |
| 5a       | 483      | 82/91 | 2.56   | 2.38 | 0.18  | -      |       |         |       |
| 5b       | 486      | 81/86 | 2.55   | 2.38 | 0.17  | -      |       |         |       |
| 6a       | 477      | 19/26 | 2.55   | 2.38 | 0.17  | -      |       |         |       |
| 6b       | 481      | 18/24 | 2.51   | 2.38 | 0.13  | -      |       |         |       |
| m-AC-DBNA| 569      | 58/89 | -      | -    | -    | 0.009  | 7.6   | 2.6     | [56] |
| p-AC-DBNA| 557      | 96/96 | -      | -    | -    | 0.009  | 1.5   | 1.2     | [56] |
| m’-AC-DBNA| 568     | 51/87 | -      | -    | -    | 0.03   | 7.8   | 8.4     | [56] |
| TDBA-Ac  | 458      | 50/83 | -93    | 3.11 | 3.05 | 0.06   | 1.0   | 9.9     | [57] |
| TDBA-Di  | 456      | 55/89 | -99    | 3.06 | 2.95 | 0.11   | 6.2   | 10.8    | [57] |
| OBA-O    | 444      | 76/84 | 3.15   | 3.06 | 0.09  | 4.1   | 4.3   | 10.5    | [58] |
| OBA-S    | 456      | 63/75 | 3.17   | 3.08 | 0.09  | 4.8   | 2.8   | 10.8    | [58] |
| OBA-BrO  | 470      | 84/92 | 3.25   | 3.21 | 0.04  | 3.7   | 9.0   | 10.5    | [58] |
| OBA-BrS  | 478      | 33/35 | 3.19   | 3.12 | 0.07  | 0.8   | 8.4   | 10.8    | [58] |
| 3CzTB    | 433      | -49   | -88    | 3.16 | 2.93 | 0.23   | 9.3   | 1.0     | [59] |
| M3CzB    | 445      | -42   | -93    | 3.06 | 2.92 | 0.14   | 7.8   | 1.4     | [59] |
| QAO      | 466      | 32/72 | -      | -    | -    | 0.18   | 93.3  | -       | [60] |
| QAO-DAD  | 548      | 49/90 | -      | -    | -    | 0.07   | 7.8   | -       | [60] |
| 3-Ph-QAD | 466      | 30/55 | -73    | 2.60 | 2.42 | 0.18   | 250   | 1.2     | [62] |
Table 1. Continued.

| Compound     | λpSol/film [nm] | FWHMsol/film [nm] | ΦPL sol/film [%] | S1 [eV] | T1 [eV] | ΔEEF [eV] | τph [μs] | kisc [s⁻¹] | Ref. |
|--------------|-----------------|-------------------|------------------|---------|---------|-----------|---------|-----------|------|
| 7-Ph-QAD     | 472 ± 2        | 22/58             | 78/78            | 2.63    | 2.44    | 0.19      | 474     | 6.4 × 10⁶   | [62] |
| DiKta        | 473 ± 2        | 27/37             | 26/75            | 2.75    | 2.55    | 0.20      | 15      | 4.6 × 10⁶   | [63] |
| Mes2DiKta    | 472 ± 2        | 29/37             | 37/80            | 2.67    | 2.46    | 0.21      | 20      | 3.1 × 10⁶   | [63] |

*Photoluminescence emission maxima; *n) Full width half-maxima from the PL spectrum; *m) Absolute photoluminescence quantum yield; *l) Estimated energy level of the S1 state from fluorescence maximum at 77 K; *k) Estimated energy level of the T1 state from phosphorescence maximum at 77 K; *j) Energy difference between singlet and triplet excited states determined from fluorescence and phosphorescence emission maxima at 77 K; *i) Lifetimes calculated from the fluorescence decay; *h) Reverse intersystem crossing decay rate from T1 to S1; *g) Obtained in 1 wt% emitter in PMMA; *f) Obtained in 1 wt% DABNA-OAr; *e) Obtained in 6 wt% doped in mCP/BCB; *d) Obtained in 10−5 m THF; *c) Obtained in 5 wt% doped in BCPO; *b) Determined from the Arrhenius plot for kisc; *a) Obtained in 10−5 m toluene; *s) Obtained in 5 wt% doped in DBFPO; *r) Obtained in 10 wt% doped in mCP; *q) Obtained in 10 wt% doped in mCP; *p) Obtained in 5 wt% CBP; *o) Obtained in 2 wt% doped in mCP; *n) Obtained in 3.5 wt% doped in mCP.

from para to the donor oxygen atoms (2b) to meta to the donor oxygen in 2c. However, this shift of phenyl substitution pattern significantly redshifted the phosphorescence maxima, and in the case of 2c, resulted in a large ΔEEF (0.31 eV) compared to 2b (0.21 eV). Finally, this multiscore core was connected to a strong electron-donating phenoxazine unit to generate 2e, that behaved as a typical D–A TADF molecule. It is not surprising that 2e showed the largest full width at half-maximum (FWHM = 96 nm) and redshift of emission (λp = 492 nm) compared to the parent molecule, 2a (λp = 398 nm, FWHM = 34 nm) in DCM. Surprisingly, given a ΔEEF of only 0.06 eV, the ΦPL is very high at 92% and the combination of these two properties was noted to be extremely beneficial to have in a TADF emitter.[10] In the same report, the authors synthesized a boron-fused benzo[6]helicene (4) from 1,3-bis[naphthalen-2-yloxy]benzene in 33%. Notably, the unsymmetrical isomer was formed only in 2% yield (not isolated). The photophysical characterization was unfortunately not provided in the original report.

The potential of these high triplet energy compounds as host materials in vacuum-deposited OLEDs was demonstrated using a well-known phosphorescent green emitter fac-Ir(ppy)3, with performance compared to that of a device using the widely used host (CBP).[28] Device performances are given in Table 2. Fused planar ring compounds are known to show aggregation in the solid state. In the case of 2a and 2b, these tended to crystallize rapidly in thin film, which ruled them out as host materials. It is somewhat surprising that 2b showed tendency to crystalize, but this was not the case with 2c and 2d. The fabricated devices with 2c and 2d acting as hosts outperformed the devices using CBP in terms of driving voltage, current efficiency, power efficiency and external quantum efficiency, and a more importantly, the device lifetime.[28] For the device stack ITO (100 nm)/dipropylcarbazole(2,3-f:2',3'-h)quinoline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) (10 nm)/N,N',N'-4,4'-tetra(1,1'-biphenyl)-4-yl)-[1,1'-biph-phenylene]-4,4'-diamine (TBBD) (60 nm)/tris(4-carbazoyl-9-yl)amine (TCTA) (10 nm)/5 wt% fac-Ir(ppy)3, in 2c or 2d (30 nm)/3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TBPB) (50 nm)/LiF (1 nm)/Al (100 nm), the lifetimes, LT50 (LT50 = the time for the luminance to decay to 80% of the initial luminance, defined in this case as 2000 cd m−2) for the OLEDs employing 2c and 2d were 1000 and 383 h, respectively, while LT50 for the OLED using CBP in the device configuration ITO/HAT-CN/TCTA/5 wt% fac-Ir(ppy)3 in CBP/TBPB/LiF/Al was only 95 h. The hosts 2c and 2d outperformed CBP in terms of current efficiency (ηc), power efficiency (ηp) and external quantum efficiency at 1000 cd m−2 (EQE1000). The EQEs at 1000 cd m−2 were 20.1%, 20.6%, and 17.6% for devices based on 2c, 2d, and CBP, respectively. The corresponding ηc and ηp values at 1000 cd m−2 were 72.1 cd A−1 and 43.5 lm W−1 for 2c, 73.8 cd A−1 and 41.9 lm W−1 for 2d, and finally, 63.3 cd A−1 and 34.1 lm W−1 for devices based on CBP. Surprisingly, when 2e was the emitter and using a different device stack architecture with the primary difference being the use of 20 wt% doping of the emitter, the LT50 was poor at less than 1 h, regardless of choice of host material: 2c or CBP. However, 2c worked better than CBP in this case too. The EQE1000 for these devices with 2c and CBP as hosts were 15.2% and 13.9%, respectively. The current and power efficiency were noted to be 52.8 cd A−1 and 36.0 lm W−1 for devices with 2c as host at 1000 cd m−2.

In 2016, Hatakayama et al. introduced related MR-TADF compounds, replacing the oxygen donor atoms for tricoordinate nitrogen atoms.[27a] The use of the more Lewis basic nitrogen atom donors produced a desired redshift of the emission in this new series of compounds. Emission remained narrow and ΔEEF remained small, thus conserving the TADF character of these nitrogen-containing emitters. Typically, color filters and/or an optical micro cavity are used in order to improve color purity in commercial displays to compensate for the broad emission profile. It is therefore not surprising that these narrow-band emitters have attracted much attention in OLED research as these optical compensation tools would no longer be needed. More importantly, with this evolved design strategy a family of deep blue emitters now became accessible. The molecular structure consists of a triphenylboron core and incorporating two nitrogen atoms that are each phenyl substituted para to the central boron atom (Figure 3).

The initial report contained two structurally related emitters, DABNA-1 and DABNA-2, where the primary difference between the two is an appended diphenylamine group and two phenyl substituents. Just like its oxygen-containing analogs, the opposing resonance effects of nitrogen donor and boron acceptor atoms separate HOMO and LUMO electron density distributions, leading to small ΔEEF and large oscillation strength for the S1→S0 transition. The synthesis of these two compounds relied on the same boron cyclization protocol previously employed (insertion of boron and cyclization).[28]
starting with a lithium-chloride exchange reaction followed by trans-metalation to boron and then electrophilic arene borylation. 

Scheme 1. DABNA-1 was synthesized in two steps from a commercially available starting material in 21% overall yield while for DABNA-2, the synthesis involved three steps and the product was obtained in 22% overall yield. The robustness and scalability of the synthetic protocol was demonstrated by carrying out gram-scale reactions. In dilute CH$_2$Cl$_2$ solutions both emitters exhibited narrow emission with $\lambda_{EL}$ of 462 and 470 nm, respectively, for DABNA-1.
and DABNA-2 and very small FWHM of ≈33 nm. Unlike typical charge transfer D–A TADF emitters, DABNA-1 and DABNA-2 show essentially no positive solvatochromism. In fact, the emission from CH$_2$Cl$_2$ to EtOH is blueshifted by 4 and 7 nm, respectively, for DABNA-1 and DABNA-2, which clearly indicates the nonpolar character of the lowest singlet excitations. In 1 wt% DABNA-2, which clearly indicates the DABNA-1, respectively, for DABNA-1 and DABNA-2, which clearly indicates the nonpolar character of the lowest singlet excitations. In 1 wt% mCBP the Φ$_{PL}$ values of these emitters remain very high at 88% and 90%, respectively, for DABNA-1 and DABNA-2. ∆$E_T$ for DABNA-1 and DABNA-2 were calculated to be 0.18 eV and 9.9 × 10$^{-3}$ s$^{-1}$, 0.14 eV, and 14.8 × 10$^{-3}$ s$^{-1}$, respectively. The presence of the substituents in DABNA-2 improves the molar absorption spectrum and also the Φ$_{PL}$ of the emitter. However, the presence of these substituents caused an undesired redshift in the emission. The delayed fluorescence lifetimes, $\tau_f$, were 93.7 and 65.3 μs DABNA-1 and DABNA-2, respectively, in 1 wt% 3,3’-bis(N-carbazolyl)-1,1’-biphenyl (mCBP) films at 300 K.

Finally, the potential of both the emitters in OLEDs were assessed in the device stack ITO (50 nm); N,N’-di(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamine (NPD) (40 nm); TCTA (15 nm); 1,3-bis(N-carbazolyl)benzene (mCP) (15 nm); 1 wt% DABNA-1 or DABNA-2 emitter; mCBP (20 nm); diphenyl-4-triphenylsilylphenylphosphine oxide (TSPO1) (40 nm); LiF (1 nm); and Al (100 nm). As expected from the photoluminescence emission measurements, DABNA-1 exhibited an emission centered at $\lambda_{EL}$ of 459 nm with an impressively small FWHM of 28 nm. Notably, these chromaticity values are of commercial relevance for displays where the CIE coordinates presented by this device (0.13, 0.09) were noted to be close to that of the National Television System Committee (NTSC) standard of (0.14, 0.08). The emission color was identified as good as that of the best values reported for fluorescent blue emitters[31] and even comparable to that of a blue emission from a color filter-assisted Samsung galaxy S5 smart phone OLED display (FWHM = 23 nm) measured for the purpose of comparison in their report. The maximum EQE, current and power efficiencies observed for the DABNA-1 device were 13.5%, 10.6 cd A$^{-1}$, and 8.3 lm W$^{-1}$, respectively, at 0.6 cd m$^{-2}$. Unfortunately, this device showed a significant efficiency roll-off at high current densities. The OLED performance with DABNA-2 was impressive with an EQE$_{max}$, current and power efficiencies of 20.2%, 21.1 cd A$^{-1}$, and 15.1 lm W$^{-1}$, respectively, at 3.2 cd m$^{-2}$; similar to the DABNA-1 device, efficiency roll-off was severe with EQE$_{300}$ of 13.4% at 100 cd m$^{-2}$ with corresponding current and power efficiencies values of 14.2 cd A$^{-1}$ and 79 lm A$^{-1}$. The maximum IQE of the OLED with DABNA-2 was determined to be nearly 100%, which indicates the success of the design strategy and the high TADF efficiency in the device compare to its parent core. Compared to the OLED with DABNA-1 the device with DABNA-2 exhibited a slight redshift of the EL spectrum ($\lambda_{EL}$ = 467 nm, CIE = 0.12, 0.13); however, the FWHM remained very narrow (28 nm) as was the case for its PL spectrum. The authors also fabricated DABNA-2 devices with a higher doping concentration of emitter from 1 to 5 wt%, which showed a slight increase in device performance coupled with a redshift in the emission ($\lambda_{EL}$ = 471 nm, CIE = 0.12, 0.17). The EQE$_{max}$, current efficiency, and power efficiencies are 20.0%, 23.8 cd A$^{-1}$,

![Chemical structures, photophysical properties, and device performances of DABNA-1 and DABNA-2. Adapted with permission.][27a] Copyright 2016, Wiley-VCH.
and 170 lm W⁻¹ at 4.1 cd m⁻² and of 14.8%, 18.0 cd A⁻¹, and 10.1 lm W⁻¹ at 100 cd m⁻², respectively. DABNA-1 and DABNA-2 were also investigated as organic semiconductor laser materials in another report and these multiresonant emitters achieved light amplification better than phosphorescent or even conventional D–A TADF systems. DABNA-2 presented a large stimulated emission cross-section and also a favorable window for light amplification. A codeposited film of 6 wt% of DABNA-2 in mCBP showed a nonlinear increase of emission intensity and a decrease of emission band width with increase in excitation intensity due to light amplification.

Following their pioneering DABNA series, the same group prepared a deep-blue-emitting boron-centered 4.8.12-triazatriangulene (also denoted as 2a; Figure 4). The versatility of the synthesis of these triazatriangulene compounds is demonstrated by the synthesis of related boron-, phosphorus-, and silicon-centered derivatives. The boron-centered triangulene 2a (Figure 4) was synthesized in five steps again employing the same key boron insertion and cyclization steps in a one-pot cascade reaction in 11% overall yield. Compound 2a (Figure 4) exhibited excellent thermal and chemical stability toward, oxygen, 1 N HCl, and 1 N NaOH. The planar nature of 2a (Figure 4) was revealed by single crystal X-ray diffraction analysis (total C-B-C bond angle = 339.9°). In addition, the B–C bonds in 2a (1.478(7)–1.480(11) Å) are much shorter than typical triaryl boranes such as Ph₃B (1.571–1.589 Å). The emission spectrum of 2a (Figure 4) in a 1 w% PMMA film showed a narrow emission band at 399 nm (ΦPL = 54%) with a remarkably high triplet energy (Eᵣ = 2.90 eV) and a small ∆EST of 0.21 eV. As with the DABNA series, the FWHM for this emission was only 26 nm, which was attributed to the rigid, fused structure. Notably, the increase in the number of donor/acceptor nitrogen atoms surrounding the central boron does not red-shift the emission spectrum of 2a (Figure 4) as compared to DABNA-1 (λPL = 460 nm in 1 wt% mCP). Quite the contrary, the λPL of 2a (Figure 4) was significantly blueshifted. In classical TADF compounds, the number of donors and acceptors has a significant influence on both the energies of S₁ and ∆EST, while in MR-TADF compounds, this is not the case. When the boron atom is replaced by phosphorus (2b) or silicon (2c), the resulting compounds lose their planarity and thus emission becomes weak. Both 2b and 2c adopt a bowl-shaped structure in the packed crystal. No devices were fabricated with any of the compounds presented a large stimulated emission cross-section and also a favorable window for light amplification.

An oxygen analog of 2a (Figure 4) was reported by Oi and co-workers in 2016. Compound 1 was obtained following a five-step reaction sequence. Insertion of boron and subsequent cyclization was conducted in one-pot synthesis, which proceeds in 22% isolated yield. The structure of 1 (Figure 4) closely resembles that of 2a (Figure 4) with a total O–B–C bond angle of 360° and very short C–B bond lengths (1.459–1.461 Å). Further, their photophysics is remarkably similar to 1 (Figure 4) showing deep-blue emission (λPL = 386 nm, ΦPL = 63, toluene), high triplet energy (ΔEST, Phos = 400–414 nm), as well as high chemical and thermal stabilities. Surprisingly, however, no delayed emission was observed in the time-resolved PL spectrum. Further, the emission spectrum of 1 (Figure 4) was significantly broader (FWHM = 48 nm) and showed a larger Stokes shift (47 nm); no devices were fabricated in this report.

In 2018, Hatakemaya’s group introduced a simplified borylation reaction by demonstrating selective double and triple borylation of triarylamines via intra- and intermolecular bora Friedel Crafts-type reactions (Scheme 2). This reaction protocol enabled the conversion of 11 C–H bonds to C–B bonds in one shot, a feat that was impossible to achieve using their previously reported methodology. The compound B2 (Figure 5) was prepared in 76% isolated yield by refluxing triarylamine in BCl₃ and no HI from the reaction mixture, which thereby inhibits the undesired retro-Friedel–Crafts reaction. Just like other structurally constrained boron-containing aromatic fused ring compounds, B2–B4 showed enhanced chemical and thermal stability. Using the same synthetic protocol, the authors were successful in borylating an electron-deficient fluorine-substituted...
substrate (B2-F; Figure 6). Double borylation of the substrate took place at 200 °C in good yields (58%); however, it was not possible to triply or quadruply borylate the substrate, even at 240 °C. Single crystal X-ray diffraction analysis reveals that B3 has a triple helical structure. Due to a large difference between the C–B and C–N bond lengths and the methyl substituents, B3 exhibited D3 symmetry, which is in contrast to the all carbon analog (hexabenzo[a,d,g,j,m,p]coronene that presents D 3d symmetry).[29a] The dihedral angle between peripheral benzene rings (30.3°–48.2°) exhibited a wider range when compared to the all carbon analog (43°–45°). Nucleus-independent chemical shifts (NICS) values indicate that the central benzene in B3 has similar aromatic character to the central benzene in hexabenzo[a,d,g,j,m,p]coronene, while all the neighboring six rings have antiaromatic character.

The photophysical properties of B2-B4 were investigated in 1 wt% PMMA. The absorption maximum of the lowest energy band of B3 (λabs = 396 nm) is significantly blueshifted from those of B2 (λabs = 438 nm), B2-F (λabs = 437 nm) and B4 (λabs = 440 nm). From the reported time-dependent density functional theory (TD-DFT) calculations, this band was identified as originating from S0–S3 and S0–S4 transitions, which are degenerate and spin-allowed (f = 0.5200), while the lower-energy S0–S2 transitions are very weak (f = 0.0006). All the emitters exhibited narrow blue emission at λPL of 455, 467, 441, and 450 nm, respectively, for B2, B2-F, B3, and B4. The emitter B2 exhibited the smallest FWHM of 32 nm (λPL = 455 nm); when this structure is functionalized with fluorine atoms, B2-F, the emission broadens (FWHM = 44 nm) and redshifted by 17 nm. The emission of B3 is the bluest in the series, but unfortunately also possesses the lowest ΦPL of 33%. The ΔEST values, determined from the energy difference between the room temperature fluorescence and 77 K phosphorescence spectra, are all sufficiently small (ΔEST ranging from 0.15 to 0.19 eV) to promote rISC. Notably, the PL spectra of B2 and B3 exhibited CIE coordinates of (0.14, 0.08) and (0.15, 0.06), respectively, which satisfy the requirements for blue emission defined by NTSC (0.14, 0.08) and the European Broadcasting Union, EBU (0.15, 0.06).

The potential of these blue TADF emitters in EL devices was demonstrated by applying B2 as the emitter in the OLED stack ITO (50 nm); NPD (40 nm); TCTA (15 nm); mCP (15 nm); 1 wt% B2 in mCBP (20 nm); TSPO1 (40 nm); LiF (1 nm); Al (100 nm). As expected from the PL measurements, the OLED with B2 showed deep blue emission with a high EQE max of 18.3% at 1 cd m−2, which fell to 12.6% at 100 cd m−2. Compared to the PL spectrum there was a 5 nm redshift coupled with a minor broadening (FWHM = 37 nm) of the EL spectrum. The corresponding CIE coordinates are (0.13, 0.11), which
are slightly redshifted compared to the CIE coordinates of (0.14, 0.08) in PMMA thin film. At 100 cd m\(^{-2}\), the \(\eta_c\) and \(\eta_d\) were noted to be 11.5 cd A\(^{-1}\) and 71 lm W\(^{-1}\). The color purity of the device is generally excellent, though the maximum luminance achieved was suboptimal at <1000 cd m\(^{-2}\).

In 2018, Huang and co-workers\(^{36}\) modified the structure of DABNA-1 by incorporating a donor carbazole unit para to the boron acceptor (TBN-TPA; Figure 6) in order to improve the efficiency of the OLED. In their previous report, Hatakeyama et al. demonstrated how the multiresonant core of DABNA-1 can be modified to improve its emission properties by functionalization with phenyl units and a diphenylamine moiety to generate DABNA-2. At the expense of color purity, they achieved a significant improvement in the PL and EL performance. The chemical structures, photophysical properties, and device performances of DABNA-1, DABNA-2, and t-DABNA are shown in Figure 6.

Later, Lee and co-workers have introduced t-DABNA, a modified version of DABNA-1 with tert-butyl groups located para to the nitrogen atoms.\(^{38}\) Following Hatakeyama's reported synthesis, t-DABNA was synthesized in two steps and in similar yields to that of the original report.\(^{27a}\) The authors aimed at reducing the severe efficiency roll-off experienced by DABNA-type molecules, and especially DABNA-1, in devices. The introduction of the tert-butyl groups was expected to reduce intermolecular interactions in the emissive layer, thereby reducing the aggregation-caused quenching that is frequently observed in thin films of these materials at more elevated doping concentrations. The t-DABNA exhibited similar photophysical properties to the parent DABNA-1, but showing an expected modest redshift of 5 nm in the emission maximum. The \(\Delta E_{ST}\) is slightly smaller for t-DABNA (0.17 eV) compared to that of DABNA-1 (0.19 eV).\(^{27a,38}\) Initial devices were fabricated with emitter doped in DPEPO as the host. At 5 wt% emitter concentration, the OLEDs with t-DABNA exhibited

![Figure 6](image_url)
fluorescence intensity associated with the energy transfer. The DPEPO:
DABNA-1 triplet excitons and transfer energy to the emitter through Förster
energy transfer and either DABNA-1 or t-DABNA (Figure 6) as the emitter. DMC-DPS is a well-known efficient blue TADF compound\[^{40}\] possessing a short \(\tau_2\) (5.6 \(\mu\)s), high triplet energy (2.91 eV), a fast rISC rate (2.35 \(\times 10^5\) s\(^{-1}\)) and was chosen as the assistant dopant as its absorption spectrum overlapped with the PL spectrum of the MR-TADF compounds, providing a route for efficient energy transfer. The authors named their energy transfer mechanism TATADF (TADF-assisted TADF). The solution-processed device stack was ITO/poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/TPBi, 20 nm/mCP, 10 nm/emitting layer (25 nm)/TSPO1, 5 nm/TPBi, 20 nm/LiF, 1.5 nm/Al, 200 nm. The emitting layer structures of the t-DABNA and DABNA-1 devices consisted of DPEPO:t-DABNA and DPEPO:DABNA-1 (25 nm, 1, 3, 5, or 10 wt\%) and those of the TATADF devices were DPEPO:MCDC-DPS:t-DABNA and DPEPO:MCDC-DPS:DABNA-1 (25 nm, 30 wt\%, 1 wt\%). The devices contained 30 wt\% assistant dopant and 1 wt\% emitter employed OLEDs exhibited performances showing EQE\(_{max}\) of 31.4\% and 23.5\% at 1 cd m\(^{-2}\) employing, respectively t-DABNA and DABNA-1. Even at a luminance of 1000 cd m\(^{-2}\) the device EQE remained high at 19.8\% and 15.6\%, respectively, using t-DABNA and DABNA-1. On the other hand, DPEPO: t-DABNA/DABNA-1 based devices exhibited EQE\(_{max}\) values of 25.1\% and 18.7\%. The improved device efficiency was associated with the reduced concentration of long-lived triplet excitons in the MR-TADF emitter, which was demonstrated by studying the time-resolved PL decay analysis of films with and without the assistant dopant. The films without assistant dopant exhibited a long \(\tau_2\) while the one with assistant dopant possessed a comparatively short \(\tau_2\) coupled with a decrease in delayed fluorescence intensity associated with the energy transfer. The higher efficiency from t-DABNA based TATADF devices is in part due to its more horizontal orientation (horizontal dipole orientation ratio = 0.79) in the emissive layer. However, the transient PL analysis suggests that even with the high concentration of DMC-DPS the long-lived delayed component of the emission decay remains. A comparison of the device lifetimes at 100 cd m\(^{-2}\) was made using t-DABNA with and without assistant TADF dopant. Even though the TATADF device presented a tenfold increase in lifetime over the other device, the lifetime was only just over 30 h (\(\tau_{30}\)). According to the authors, the device lifetime can be further improved by selecting a more stable host and assistant dopant.

In an endeavor to achieve stable device using an emitter based on the DABNA core, the same group introduced another strategy wherein the DABNA core is employed as a fluorescent emitter in the OLED rather than utilizing them as TADF materials.\[^{40}\] In order to mitigate against the long delayed lifetime of TADF emitters, which has been identified as deleterious for device stability, the authors designed an energy transfer scheme that permitted quenching of the triplet excitons generated upon electrical excitation by using an anthracene based fluorescent high band gap host \(\alpha\)-AN (\(E_g = 3.15\) eV, \(E_T = 1.73\) eV).\[^{40}\] The \(E_T\) of the host \(\alpha\)-AN is lower than that of t-DABNA (\(E_g = 2.80\) eV, \(E_T = 2.63\) eV) and DABNA-1 (\(E_g = 2.82\) eV, \(E_T = 2.63\) eV) and as a consequence triplets on the emitter are back energy transferred to the fluorescent host rather than undergoing rISC to the singlet excited state of the emitter. At a doping concentration of 3 wt\% of emitter in the host, this energy transfer process dominates as indicated by a very weak emission from the host in the PL spectrum; no delayed emission was observed from the emitter. Devices were fabricated using 1–5 wt\% of emitter in the emissive layer in a Device configuration of (ITO, 50 nm)/N,N,N’-tetra(1,1’-biphenyl)-4-yl]-1,1’-biphenyl)-4,4’-diamine (BBPBA):HATCN(40 nm:30 wt\%)/BPBP (10 nm)/9,9-dimethyl-10-(9-phenyl-9-carbazol-3-yl)-9,10-dihydroacridine (PCzac) (10 nm)/\(\alpha\)-AN:DMAC-DPS (30 nm:3 wt\% emitter)/2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[d,f]uran (DBFDrz) (5 nm)/2-(4,10-dio-naphthalen-2-yl-anthracene-2-yl)-phenyl-1-phenyl-1H-benzoimidazole (ZADN) (20 nm)/LiF (1.5 nm)/Al (200 nm). A pyrene-based compound 4,4’-(pyrene-1,6-diylbis[phenylazanediyl])dibenzonitrile (PyCN) was used as a reference emitter in this case. Just like their previous report,\[^{40}\] the tert-butyl-modified DABNA-1, t-DABNA (Figure 6) performed better in OLEDs compared to DABNA-1. Blue narrow-band emission with CIE\(_y\) < 1 were achieved in the device stack. The corresponding EQE/CE at 1000 cd m\(^{-2}\) for devices based on DABNA-1, t-DABNA and PyCN were 4.9/3.4, 70/5.8, and 3.4/2.8, respectively. Device lifetime measurements at 200 cd m\(^{-2}\), revealed \(\tau_{50}\) values of 608 h for the t-DABNA device whereas for the OLEDs with DABNA-1 and PyCN lifetimes were significantly lower at 203 and 33 h respectively.

The same group continued to work on the device architecture to boost the EL performance of t-DABNA based devices. The authors introduced a phosphorescence-sensitized TADF (PSTADF) device to harvest triplet excitons without transferring energy into the triplet state of the MR-TADF emitter.\[^{42}\] This type of energy transfer process has been previously used for other TADF emitters.\[^{42}\] Unlike the previously discussed device,\[^{40}\] dark triplets are converted into singlet here. It was noted that both efficiency and device lifetime were significantly improved compared to the previous devices with t-DABNA while simultaneously maintaining its deep blue emission. Devices were fabricated with TSPO1 host with 3% t-DABNA as emitter in the device configuration ITO, 50 nm/PEDOT:PSS, 60 nm/TPAC, 20 nm/mCP, 10 nm/emitting layer, 25 nm/TSP01, 5 nm/TPBi, 20 nm/LiF, 1.5 nm/Al, 200 nm. The devices without inclusion of the phosphorescent sensitizer presented poor performance in terms of brightness (<500 cd m\(^{-2}\)) and efficiency roll off (EQE\(_{50}\) = 4.5\%). The authors investigated this energy transfer scheme with three different iridium-containing phosphorescent materials, fac-tris[1,1’-(2,6-diisopropylphenyl)-1H-imidazol-2-yl]benzotriazole]iridium (CNIImIr),\[^{43}\] fac-tris(1,1’-(2,6-diisopropylphenyl)-2-(4-fluorophenyl)-1H-imidazole]iridium (F-Ir),\[^{43}\] and fac-tris(5-(tertbuty)-1,3-diphenyl-2,3-dihydro-1H-imidazo[4,5-b]pyrazine]iridium (Ir(cb)).\[^{43}\] The best sensitizer for t-DABNA was identified as Ir(cb) from the favorable spectral overlap of sensitizer emission.

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and the absorption of t-DABNA. Complete energy transfer occurred in this series and only emission from t-DABNA was observed. This is also reflected in the fabricated device with an Ir(cb)\textsubscript{3} concentration of 30 wt% and t-DABNA doping at 0.5, 1, and 2 wt%. Pure blue emission with a CIE\textsubscript{y} of (0.13, 0.13) resulted from all the device in this series. Devices with other phosphorescent sensitzers exhibited mixed emission from the sensitizer and the MR-TADF emitter. The maximum luminescence noted for the best device (0.5 wt% t-DABNA) was 5019 cd m\textsuperscript{-2}. The EQE/CE/PE for devices with 0.5, 1, and 2 wt% emitter at 1000 cd m\textsuperscript{-2} were 19.4%/18.7 cd A\textsuperscript{-1}/9.7 lm W\textsuperscript{-1}, 18.4%/16.7 cd A\textsuperscript{-1}/8.5 lm W\textsuperscript{-1}, and 16.3%/14.5 cd A\textsuperscript{-1}/70 lm W\textsuperscript{-1}, respectively. For the lifetime studies, TSPO1 host was replaced with the more stable mCBP host, and the emitter doping concentration was set to 1 wt%. The EQE was slightly reduced to 14.2% at 1000 cd m\textsuperscript{-2}. The LT\textsubscript{50} was measured to be 293 h at 200 cd m\textsuperscript{-2}. The device stability was found to be significantly higher for the TATADF devices introduced in their earlier report,\cite{28} which indicates further efforts are required to obtain both stable OLEDs at high efficiencies when employing MR-TADF emitters.

Expanding beyond triangulene structures is the recent report by Hatakeyama and co-workers of a pseudolinear MR-TADF compound, v-DABNA (Figure 7).\cite{29} Notably, the FWHM of v-DABNA is just only 14 nm in toluene, which is the narrowest of all the MR-TADF compounds reported so far. The extremely narrow emission band is attributed to the weak vibronic coupling to stretching modes in the S\textsubscript{1} excited state, so that the ground and excited states actually feature similar equilibrium geometries. The emission color of this compound is similar to those of the DABNA series of emitters previously reported by the same group. This molecule was synthesized in three steps in good yields in a similar manner to their previous report.\cite{29a} This report also introduces a new oxygen-bridged boron-centered high band gap host (DOBNA-OAr) for v-DABNA, which is itself based on the previously reported structure of 2a (Figure 2). In dilute toluene solution, the emission maximum of the host is \( \lambda_{\text{PL}} = 388 \text{~nm} \) (FWHM = 34) with an associated high \( \Phi_{\text{PL}} \) of 65%. The absolute \( \Phi_{\text{PL}} \) of a 1 wt% doped film of v-DABNA in DOBNA-OAr is 90%, which is higher than that of v-DABNA in dilute toluene solutions (74%). The \( \Delta E_{\text{ST}} \) value of v-DABNA is miniscule at only 0.017 eV, which is the smallest among MR-TADF compounds reported to date. The calculated \( k_{\text{RISC}} \) and \( k_{\text{ISC}} \) from the transient decay spectra of v-DABNA in doped film are, respectively, \( 2.0 \times 10^6 \), \( 2.2 \times 10^7 \), \( 2.3 \times 10^8 \), and \( 2.0 \times 10^9 \) s\textsuperscript{-1}. Strikingly, there is an approximate 20- and 13-fold improvement in the \( k_{\text{RISC}} \) noted for v-DABNA versus DABNA-1 and DABNA-2, respectively, which is the result of the significantly smaller \( \Delta E_{\text{ST}} \) (0.017 eV). From an Arrhenius analysis\cite{30} of \( k_{\text{RISC}} \) versus 1/T, the activation energy for RISC was estimated to be 0.07 eV, which is higher than the calculated \( \Delta E_{\text{ST}} \) determined from the steady-state fluorescence and phosphorescence spectra, indicating a potential contribution of higher triplet energy levels (\( T_2 \)) aiding the RISC process in v-DABNA.\cite{31,32} It is noteworthy that this emitter presented a very short delayed lifetime (\( \tau = 4.1 \text{~ns and} \tau_{\text{TADF}} = 4.1 \text{~µs} \)).

The OLED with a device structure of ITO, 50 nm/NPD, 40 nm/TCTA, 15 nm/mCP, 15 nm/1 wt% v-DABNA in DOBNA-OAr, 20 nm/TSPO1, 30 nm/LiF, 1 nm/Al, 100 nm showed pure blue emission (\( \lambda_{\text{EL}} = 469 \text{~nm} \)) with a record small FWHM of only 18 nm. The corresponding CIE coordinates are (0.12, 0.11). Strikingly, the device showed excellent efficiencies with an EQE\textsubscript{max} of 34.4% at a luminance of 15 cd m\textsuperscript{-2}. The efficiency roll-off was also much lower than those of most MR-TADF-based devices with EQEs of 32.8% and 26.0% at 100 and 1000 cd m\textsuperscript{-2}, respectively, corresponding to an efficiency drop of 1.6% and 8.6% at 100 and 1000 cd m\textsuperscript{-2}, respectively. The impressive performance of the OLED suggests that bimolecular quenching processes such as triplet-triplet and singlet–triplet annihilation are largely suppressed. Unfortunately, the emission intensity is drastically reduced after 31 h, but without spectral change, and thus efforts are still required to improve the device performance.

This blue emitter (v-DABNA) was utilized in a different way by Adachi and co-workers in an exciplex-forming OLED device through an exciton recycling strategy.\cite{33} The role of v-DABNA in this case was to act as a fluorescent emitter for a TADF acceptor-based exciplex-forming host. The main focus of this report was to demonstrate the exciton recycling efficiency of their exciplex-forming host rather than utilizing the TADF property of v-DABNA. Even though the efficiency of doped devices (1 wt% v-DABNA in 49.5 wt% Tris-PcZ:49.5 wt% 3Cz-TRZ) was higher (EQE\textsubscript{max} = 19%) than that of nondoped devices, the overall device performance was inferior to that of the original v-DABNA-based device developed by Hatakeyama et al. This exciplex device also suffered from a significant emission redshift (CIE\textsubscript{y} = 0.36) and band-broadening (FWHM = 50 nm) compared to the pure blue emission based on the original v-DABNA device. The v-DABNA doped exciplex device lifetime was 300 h (LT\textsubscript{50}) at a high luminescence of 1260 cd m\textsuperscript{-2}.

![Figure 7. Chemical structures, photophysical properties, and device performances of v-DABNA and DOBNA-OAr. Adapted with permission.](https://www.afm-journal.de)
A new series of B,N-doped nanographenes with a more extended π-conjugation than exists in DABNA series was recently reported by Duan and co-workers. The design includes the replacement of diphenyl amine units in DABNA-1 with tert-butyl carbazole (Figure 8 and the incorporation of iso-meric fluorobenzene electron-withdrawing units. 2F-BN, 3F-BN, and 4F-BN were synthesized following previous reports. Introduction of the fluorobenzene groups induces a charge transfer character to the HOMO-LUMO transition. Owing to the rigid structural framework, the devices fabricated with these new emitters also exhibited excimer emission. The OLEDs using each of these three emitters showed small efficiency roll-off. The EQE_{5000} are 15.0%, 21.1%, and 16.4% for 2F-BN, 3FBN, and 4F-BN, respectively. The OLEDs showed lifetimes (LT_{90}) of 45.76, 15.53, and 10.35 h for 2F-BN, 3F-BN, and 4F-BN, respectively, at a high initial luminescence of 2000 cd m^{-2}.

Inspired from the results of our computational studies (vide infra) on linear MR-TADF compounds, we designed and synthesized a deep blue-emitting, linear, ladder type B,N doped heptacene (α-BNOH) and investigated its photophysical properties (Figure 9). B,N-doped ladder-type acenes had been previously identified as highly fluorescent materials by Agou et al. However, the previous report did not recognize that these compounds fall within the family of MR-TADF emitters. α-BNOH was obtained from a one pot triple electrophilic borylation at high temperature using a similar protocol to the one developed by Hatakeyama and co-workers[29]. High thermal stability was observed for α-BNOH (T_{g} = 554 °C). The λ_{PL} is 390 nm with a narrow FWHM of 31 nm in THF solutions, φ_{PL} under N_{2} is 50%. Unlike v-DABNA or other MR-TADF emitters, ΔE_{ST} for this emitter was found to be on the higher side (0.31 eV) in solution. Temperature-dependent PL decay measurements indicated that aggregates are formed at low temperature in THF glass, which facilitates delayed emission from a TTA process. This is surprising considering that the emission measurements were done at very high dilution. The TADF component becomes dominant at 300 K. Direct determination of the emitters also exhibited good device performances, with EQE_{max} (PE_{max}) values of 22.0 (69.8 lm W^{-1}) and 22.7 (72.3 lm W^{-1}) and 20.9% (51.3 lm W^{-1}) for 2F-BN, 3F-BN, and 4F-BN, respectively.
activation energy for the delayed emission is only 70 meV while the \( \Delta E_{ST} \) was calculated to be 310 meV. Similar behavior was observed in other TADF reports including for \( \nu\)-DABNA. This dichotomy can be explained by invoking contributions from higher-lying triplet states to the RISC process, which is supported by our computations. The delayed lifetime in solution was found to be the shortest (0.45 \( \mu \)s) of all the MR-TADF emitters reported to date. In 1 wt% PMMA film of 10−3BNOH, \( \tau_d \) is 165 and 147 \( \mu \)s for ADBNA-Me-Mes and ADBNA-Me-Tip, respectively. The delayed lifetimes, \( \tau_d \), are 165 and 147 \( \mu \)s for ADBNA-Me-Mes and ADBNA-Me-Tip, respectively. The \( k_{RISC} \) values for ADBNA-Mes (7.6 \( \times \) 10^3 s\(^{-1}\)) and ADBNA-Me-Tip (9.0 \( \times \) 10^3 s\(^{-1}\)) were noted to be similar to that of DABNA-I (11.1 \( \times \) 10^3 s\(^{-1}\)). Compared to the pseudolinear diboron MR-TADF emitter \( \nu\)-DABNA, the triangulene-based diboron emitters exhibited very long delayed fluorescence lifetimes in the same host with a similar \( \Phi_{PL} \) values.

Devices were fabricated using the same host as for \( \nu\)-DABNA, in the following architecture: ITO 50 nm/HAT-CN, 5 nm/NPB, 35 nm/TCTA, 15 nm/mCP, 15 nm/1 wt% ADBNA emitter and 99 wt% DOBNA-OAr, 20 nm/TSP01, 40 nm/LIF, 1 nm/Al, 100 nm. The OLEDs showed narrow-band sky-blue emission of 481 nm (FWHM = 32 nm) and 480 nm (FWHM = 33 nm), respectively for ADBNA-Me-Mes and ADBNA-Me-Tip. The corresponding CIE values are (0.10, 0.27) and (0.11, 0.29) for ADBNA-Me-Mes and ADBNA-Me-Tip, respectively. Notably, the device with ADBNA-Me-Tip showed an EQE\(_{\text{max}}\) of 21.4%, while with ADBNA-Me-Mes showed a slightly lower value of 16.2%. The improved efficiency of the device with ADBNA-Me-Tip was rationalized from its higher orientation parameter (S) of –0.40 versus –0.11 of ADBNA-Me-Mes based on angle-dependence PL measurements. However, the maximum brightness achieved with these devices are low, less than 1000 cd m\(^{-2}\). Here too, large efficiency roll-offs were observed.

Recently, Wang and co-workers reported a series of emitters based on an inverted DABNA design where the nitrogen donor is positioned centrally in the triangulene structure (Figure 11), structures that are similar to the ADBNA series reported by Hatakeyama and co-workers. Synthesis was not as straightforward as previously reported MR-TADF emitters, with...
direct conversion of $\text{N}(\text{B-tolyl})_3$ to the target not possible with simple trans-metallation and insertion. Instead intermediate 1 (Scheme 4) was isolated and was subjected to borylation with BBr$_3$ to afford asymmetric intermediate 2a and symmetric analog 2b, the product ratio of which could be controlled by the stoichiometry of BBr$_3$ and the reaction times (Scheme 5). Using this protocol, a number of derivatives were synthesized (Figure 11). Previous attempts to make inverted DABNA-type structures are limited to symmetrical structures while the synthetic route developed in this report successfully generates unsymmetrical inverted DABNA derivatives. Compounds 3–5b displayed PL features reminiscent of MR-TADF, showing narrow FWHM, and only a small degree of positive solvatochromism. Emission maxima ranged from 482 to 487 nm, and $\Phi_{PL}$ ranged from 71% to 88%. The family of emitters showed $\Delta E_{ST}$ of between 0.17 and 0.19 eV. A different story exists for 6a and 6b. Here, in DCM, two emission peaks were observed, one located at 477/481 and 609/601 nm, respectively. The bluer emission band is much more MR-TADF in nature, with narrow emission and moderate solvatochromism, whereas the low

\begin{align*}
\text{Scheme 3. Synthesis of inverted ADBNA derivatives: a) NBS (3.1 equiv.) CH$_3$CN, rt, 20 h, b) t-BuLi (6.1 equiv.) t-Bu-benzene, \text{–40 °C} to rt, rt 1 h, c) BBr$_3$ (2.0 equiv.), 0 °C to rt, rt 1 h, d) 1,2,2,6,6-pentamethyipiperidine (2.0 equiv.), rt to 160 °C, 160 °C 15 h, and e) ArMgBr (3.0 equiv.), rt. Adapted with permission.}^{[54]} \text{Copyright 2019, American Chemical Society.}
\end{align*}

Figure 11. Chemical structures and photophysical properties of 3, 4a, 4b, 5a, 5b, 6a, and 6b. Adapted with permission.\textsuperscript{[55]} Copyright 2020, Wiley-VCH.
energy emission band is more characteristic of that observed for CT type D–A materials. It is unclear at present why dual emission was observed only in these two compounds and not the others in the family. No devices were fabricated in this report to identify the EL performances of these new emitters.

The impact of the initial reports of MR-TADF compounds has spurred increased research efforts to design new MR-TADF emitters and donor–acceptor derivatives that rely on MR-TADF motifs which act as acceptor groups. One of such recent report by Meng et al.[56] employs 2a (Figure 2), previously reported by Hatakeyama and co-workers, as acceptor for donor–acceptor TADF emitters, in a similar design paradigm to that of 2e (Figure 2), which used a phenoxazine donor.[28] The authors synthesized three regioisomers (Figure 12) having the same acceptor core (2a; Figure 2) and containing two electron donor units (dimethylacridine, DMAc). The impact of the position of donor substitution on the TADF properties were investigated: m-AC-DBNA (meta to boron and para to oxygen), p-AC-DBNA (para to boron and meta to oxygen) and m'-AC-DBNA (meta to boron and ortho to oxygen). p-AC-DBNA showed the highest temperature stability (T_d = 445 °C) and melting point (T_m = 436 °C) along with the highest Φ_PL (96%) and shortest τ_d (1.17 µs) in CH_2Cl_2 among the family of isomeric emitters; this isomer also showed the fastest k_RISC rate (1.2 × 10^5 s^-1) in 5 wt% doped BCPO films. Surprisingly, the emission maxima remain similar (λ_PL = 496 nm) compared to m-AC-DBNA (λ_PL = 492 nm) and m'-AC-DBNA (λ_PL = 498 nm) in doped film. As expected from their PL measurements, the OLED with

![Scheme 4. Synthesis of inverted DABNA derivatives: a) t-BuLi, MesB(OMe)_2, THF, -78 °C, Route A: a) BBr_3 (1 equiv.), toluene, 110 °C, 1 h, b) Li–Ar (1.2 equiv.), THF/Et_2O, -78 °C → RT, 12 h. Route B: a) BBr_3 (5 equiv.), toluene, 110 °C, 24 h, b) Li–Ar (2.4 equiv.), THF/Et_2O, -78 °C → RT, 12 h. Adapted with permission.[55] Copyright 2020, Wiley-VCH.](image)

![Figure 12. Chemical structures, photophysical properties, and device performances of m-AC-DBNA, p-AC-DBNA, and m'-AC-DBNA. Adapted with permission.[56] Copyright 2019, Wiley-VCH.](image)
p-AC-DBNA showed excellent EL performance in terms of turn-on voltage (3.3 V), maximum luminance (40 750 cd m \(^{-2}\)), and EQE \(_{\text{max}}\) (20.5%). Devices were fabricated in the configuration, ITO/HATCN (4.2 nm)/TAPC (34 nm)/emission layer (23 nm)/TmPyPB (21 nm)/LiF (1 nm)/Al (100 nm). Even at higher luminescence of 1000 cdm \(^{-2}\), devices based on p-AC-DBNA presented higher efficiency values (EQE = 16.4%). Due to the impressive device performance, the authors fabricated devices with different doping concentration (5–35 wt%) of emitters to identify the performance change. It was identified that 10 wt% emitter presented the best device performance in terms of efficiency. However, the maximum EQE was nearly insensitive to the doping concentration of the emitter. It is noted that at higher doping concentrations, efficiency roll off was significantly small (only 5% for 5% emitter vs 26% for 5% emitter) at the same time maximum brightness was dramatically increased (69 160 cd m \(^{-2}\) for 35% emitter vs 28 600 cd m \(^{-2}\) for 15% emitter). Impressed by the high performance of higher doping devices, this report also fabricated a nondoped device with the best device performance. The expected efficiency boost was not observed for this device as evidenced by an EQE \(_{\text{max}}\) of only 14.1 (efficiency roll off, 10%) with a maximum luminescence of 27 600 cd m \(^{-2}\).

Kwon and co-workers[57] also explored the use of p,0-MR-TADF compounds as acceptors in D–A TADF emitters (Figure 13). Two emitters were described in this report sharing the same boron-containing acceptor, a tert-butyl analog of 2a (Figure 2), with two different donors: diindolocarbazole (TDBA-DI) and dimethylcarbazine (TDBA-Ac). TD-DFT calculations suggest that in these two emitters there is strong separation of the electron densities in the HOMO and LUMO thereby affording small calculated \(\Delta_{\text{ST}}\) of 0.006 and 0.073 eV for TDBA-Ac and TDBA-DI, respectively. As expected from the molecular design, both TDBA-Ac and TDBA-DI showed blue emission in dilute toluene with small \(\Delta_{\text{ST}}\) at 458 nm (0.06 eV) and 456 nm (0.11 eV), respectively, for TDBA-Ac and TDBA-DI. Associated with the small \(\Delta_{\text{ST}}\), TDBA-Ac and TDBA-DI, respectively, possessed very short \(\tau_{\text{d}}\) of 1.0 and 6.2 \(\mu\)s in toluene. They also showed that \(\tau_{\text{d}}\) becomes shorter in more polar solvents, which is due to stabilization of the charge transfer band. Unlike MR-TADF emitters, these emitters do not show any concentration quenching when doped in films at high concentration (20 wt%). Similar values for \(k_{\text{RISC}}\) (9.9 \(\times\) 10\(^5\) and 1.1 \(\times\) 10\(^6\) s\(^{-1}\)) was inferred for TDBA-Ac and TDBA-DI, respectively. However, the nonradiative decay rate, \(k_{\text{nr}}\), of TDBA-Ac (74 \(\times\) 10\(^4\) s\(^{-1}\)) was found to be higher than that of TDBA-DI (1.1 \(\times\) 10\(^5\) s\(^{-1}\)). Both the emitters were tested in an OLED device stack having a configuration of ITO/HATCN, 7 nm/TAPC, 50 nm/DCDPA, 10 nm/20% TADF emitter:host, 25 nm/dibenzo[b,d]furan-2,8-diylbis(diphenylphosphine oxide) (DBFPO), 10 nm/TPBi, 20 nm/LiF, 1.5 nm/Al, 100 nm. A high EQE \(_{\text{max}}\) of 25.7% with a CIE of (0.14, 0.15) was observed for TDBA-Ac in the OLED using DBFPO as the host. When a less polar host such as 5-(5-(2,4,6-trisopropylphenyl)pyridin-2-yl)-5H-benzo[d] benzol[4,5]imidazo[1,2-a]imidazole (PPBI) was used in the device, the \(\Delta_{\text{EQE}}\) (448 nm) blueshifted with the EL spectrum showing CIE of (0.15, 0.06) but the OLED showed a slightly lower EQE \(_{\text{max}}\) of 21.5%. The difference in performance is more pronounced when the emitter is switched to TDBA-DI. The OLED showed EQE \(_{\text{max}}\) of 32.2% and 38.2% with PPBI and DBFPO as hosts in the emissive layer, respectively. It is noteworthy that the DBFPO/TDBA-DI device exhibited a high luminance of 47 680 cd m \(^{-2}\) and also a very low efficiency roll-off to an EQE of 25.2% at 5000 cd m \(^{-2}\). The authors demonstrated that the emitter orients horizontally in the thin film, and the improved light-outcoupling contributes to the outstanding EQEs of the OLED. The operational life (LT\(_{50}\)) of the same emitter/host system was short, less than 2 h at 500 cd m \(^{-2}\), which was improved to 102.9 h by switching to a mixed host system of mCBP-CN:DBBFT; however, this was associated with a much lower EQE \(_{\text{max}}\) of 22.3%.

Very recently, Song et al.[38] reported a series of D–π–A-type TADF emitters (Figure 14) having the same 2a acceptor (Figure 2) core reported by Hatakeyama and co-workers[28] This family of emitters contains phenoxazine and phenothiazine donor units attached to the acceptor core through a phenyl linker. Unlike other D–A system using 2a (Figure 2) as the acceptor, these molecules show different regiochemical substitution on the acceptor unit. Bromination of 2a (Figure 2) occurs on the most electron-rich central ring. The brominated intermediate was then elaborated further via Suzuki–Miyaura coupling with boronic esters of donor units. Mono- and dibromination products of 2a (Figure 2) were obtained using NBS as the bromination agent in 67% and 56% yields, respectively. The OBO-O and OBO-S emitters share the same acceptor and...
contain phenoxazine and phenothiazine donors, respectively. The OBA-BrO and OBA-BrS each contain an additional bromine substituent on the acceptor. In dilute toluene solutions, emission maxima ranged from 444 to 478 with Φ<sub>PL</sub>'s of 53–84%. In line with previously reported D–A systems, the ∆E<sub>ST</sub> values are very small, ranging from 0.04 to 0.09 eV in 10 wt% mCP films.

Devices were fabricated with the stack ITO/HATCN, 5 nm/TAPC, 40 nm/mCP, 20 nm/TmPyPB, 40 nm/LiF, 1 nm/Al, 100 nm. The best OLED was obtained with OBA-O at 5 wt% emitter doping concentration, and this device was gratifyingly also the bluest (λ<sub>EL</sub> = 446 nm, CIE = (0.17, 0.17)) of all the devices in this report. A low turn on voltage (2.7 V), high

Figure 14. Chemical structures, photophysical properties, and device performances of OBA-O, OBA-S, OBA-BrO, and OBA-BrS. Adapted with permission. Copyright 2019, Royal Society of Chemistry.

Figure 15. Chemical structures, photophysical properties, and device performance of 3CzTB and M3CzB. Adapted with permission. Copyright 2020, Royal Society of Chemistry.
The emitter (acceptors, showing clearly an LE character. It is surprising that phosphorescence spectra match with that of the corresponding substituents. From the low temperature PL measurements, the groups at the para, acceptor is selected without tert-butyl acceptor remains the same to their previous report, for the second emitter, M3CzB-butyl is disposed by Jiang and co-workers.[53] The molecule and its derivatives were previously synthesized by Venkataraman and co-workers.[51,61] However, their TADF properties were not acknowledged in the original report. In line with previous boron-containing MR-TADF compounds, the PL spectrum of QAO was blue ($\lambda_{pl} = 466 \text{ nm}$ in toluene), narrow (FWHM = 32 nm), bright ($\Phi_{pl} = 72.4\%$, 5 wt\% in mCP), and with an associated small $\Delta E_{ST}$ of 0.18 eV, properties that are very close to those observed for DABNA-I in saturated ethanol ($\lambda_{pl} = 458 \text{ nm}$, FWHM = 36 nm, $\Delta E_{ST} = 0.15 \text{ eV}$).[27a] Unlike boron-based MR-TADF compounds these ketoine-containing molecules are relatively easy to synthesize. Following the previously reported synthesis,[51,61] QOA was obtained in a good overall yield of 51%. TD-DFT calculations suggested that the $S_0\rightarrow S_1$ transition of QOA has a rather large oscillator strength of 0.157. Time-resolved PL measurements in 5 wt% doped mCP films showed a $\tau_g$ of 93.3 $\mu$s. The absolute $\Phi_{pl}$ of the doped film remained high at 72.4%. Devices were fabricated in a configuration of ITO/HAT-CN, 10 nm/TAPC, 45 nm/TCTA, 10 nm/5 wt% QAO:mCP, 20 nm/4,6-Bis(3,5-di(pyridin-4-yl)phenyl)-2-phenylpyrimidine (B3PYMPM), 40 nm/8-hydroxyquinolinolato lithium (Liq), 2 nm/Al, 120 nm. The OLED showed a low turn-on voltage of 3 V (1 cd m$^{-2}$) and a narrow emission (FWHM = 39 nm) band at $\lambda_{EL} = 468 \text{ nm}$, which, though slightly broader, essentially remains very close to the emission in solution. The CIE coordinates were ($0.13, 0.18$) and the OLED using QAO showed poorer color purity than the devices employing boron-based MR-TADF emitters. The device nonetheless exhibited high performance with maximum current efficiency ($\Phi_{max}$), power efficiency ($PE_{max}$), and EQE$_{max}$ of 26.2 cd A$^{-1}$, 31.6 lm W$^{-1}$, and 19.4%, respectively. However, the OLED also suffered from strong efficiency roll-off (56%), which may be due to the long-lived delayed lifetime and deleterious intermolecular interaction from its fused planar structure.

$\Phi_{max}$ (178% at 13.5 cd m$^{-2}$), CE (33.2 cd A$^{-1}$), PE (34.2 lm W$^{-1}$) and a high brightness (6785.2 cd m$^{-2}$) values were noted for this device. Irrespective of the concentration of the compound, all the brominated emitters performed inferior to the other devices, especially the phenothiazine derivatives.

The same group modified the resonant acceptor core 2a (Figure 2) to generate two new D–A TADF systems with tercarabazole donors with unmodified MR fragment acceptor (2a; Figure 2) exhibited $\Delta E_{ST}$ of 0.14 eV while for 3CzTB the $\Delta E_{ST}$ is 0.23 eV in toluene. Emission maxima are 433 and 445 nm, respectively, for 3CzTB and M3CzB. Similar to the previous reports, these D–A systems also possess high $\Phi_{PLS}$ (88–93%) and short delayed lifetimes (9.3–7.8 $\mu$s) in toluene solution. Devices were fabricated in the configuration ITO, 50 nm/HATCN, 7 nm/TAPC, 50 nm/DCDPA, 10 nm/20 wt% dopant in DBFPO, 25 nm/DBFPO, 5 nm/TPBi, 15 nm/LiF/Al, 1.5/100 nm. The turn-on voltages are around 3 V. The $\lambda_{EL}$ is redshifted from their corresponding $\lambda_{pl}$ in toluene solution. The device with M3CzB (18 160 cd m$^{-2}$) was brighter than that with 3CzTB (11 690 cd m$^{-2}$) and shows a slightly redshifted emission. The CIE values are (0.14, 0.19) and (0.14, 0.26) respectively for 3CzTB and M3CzB.

Corresponding EQE$_{max}$/EQE$_{1000}$/CE$_{max}$/CE$_{1000}$ values are 29.1%/13.5% (0.14, 0.10), and 14.4% (0.13, 0.19) for 3CzTB and M3CzB, respectively. Devices fabricated for lifetime measurements was significantly lower. The EQE (CIE values) values of these latter devices were 76% (0.14, 0.10), and 14.4% (0.13, 0.19) for 3CzTB and M3CzB, respectively.

Another inverted design of the DABNA series with the nitrogen atom donor placed centrally was recently reported by Jiang and co-workers.[60] The molecule QAO consisted of a triphenyl amine having two para-disposed carbonyl bridges (Figure 16). This molecule and its derivatives were previously synthesized by Venkataraman and co-workers.[51,61] However, their TADF properties were not acknowledged in the original report. In line with previous boron-containing MR-TADF compounds, the PL spectrum of QAO was blue ($\lambda_{pl} = 466$ nm in toluene), narrow (FWHM = 32 nm), bright ($\Phi_{pl} = 72.4\%$, 5 wt% in mCP), and with an associated small $\Delta E_{ST}$ of 0.18 eV, properties that are very close to those observed for DABNA-I in saturated ethanol ($\lambda_{pl} = 458$ nm, FWHM = 36 nm, $\Delta E_{ST} = 0.15$ eV).[27a] Unlike boron-based MR-TADF compounds these ketone-containing molecules are relatively easy to synthesize. Following the previously reported synthesis,[51,61] QOA was obtained in a good overall yield of 51%. TD-DFT calculations suggested that the $S_0\rightarrow S_1$ transition of QOA has a rather large oscillator strength of 0.157. Time-resolved PL measurements in 5 wt% doped mCP films showed a $\tau_g$ of 93.3 $\mu$s. The absolute $\Phi_{pl}$ of the doped film remained high at 72.4%. Devices were fabricated in a configuration of ITO/HAT-CN, 10 nm/TAPC, 45 nm/TCTA, 10 nm/5 wt% QAO:mCP, 20 nm/4,6-Bis(3,5-di(pyridin-4-yl)phenyl)-2-phenylpyrimidine (B3PYMPM), 40 nm/8-hydroxyquinolinolato lithium (Liq), 2 nm/Al, 120 nm. The OLED showed a low turn-on voltage of 3 V (1 cd m$^{-2}$) and a narrow emission (FWHM = 39 nm) band at $\lambda_{EL} = 468$ nm, which, though slightly broader, essentially remains very close to the emission in solution. The CIE coordinates were (0.13, 0.18) and the OLED using QAO showed poorer color purity than the devices employing boron-based MR-TADF emitters. The device nonetheless exhibited high performance with maximum current efficiency ($\Phi_{max}$), power efficiency ($PE_{max}$), and EQE$_{max}$ of 26.2 cd A$^{-1}$, 31.6 lm W$^{-1}$, and 19.4%, respectively. However, the OLED also suffered from strong efficiency roll-off (56%), which may be due to the long-lived delayed lifetime and deleterious intermolecular interaction from its fused planar structure.

Figure 16. Chemical structures, photophysical properties, and device performances of QAO and QAO-DAd. Adapted with permission.[60] Copyright 2019, Wiley-VCH.
The same report also used QAO core as an acceptor in a conventional donor–acceptor TADF configuration in which DMAc serves as the donor unit (QAO-DAd).[60] This structure contains two DMAc donors and a tert-butyl substituent located para to the central nitrogen atom. DFT calculations predict that the donor is twisted into an orthogonal conformation with respect to the acceptor, leading to well-separated HOMO and LUMO and a correspondingly small \( \Delta E_{CT} \) (30 \( \mu \)s, \( \Phi_{PL} \) = 73\%, FWHM 55 nm (2 wt\% mCP)) and a very small \( \Delta E_{CT} \) of 0.01 eV. As with other D–A TADF emitters, QAO-DAd exhibited broad emission associated with an ICT transition from the emissive singlet state. Both vacuum-deposited and solution-processed devices were fabricated with this emitter. Vacuum deposited devices were fabricated in the configuration ITO/HAT-CN, 10 nm/TAPC 45 nm/TCTA, 10 nm/5 wt% QAO-DAd:CBP, 20 nm/TmPyPB, 50 nm/Liq, 2 nm/Al, 120 nm. This device exhibited yellow-green emission with \( \lambda_{EL} \) of 552 nm and CIE coordinates of (0.41, 0.56). The OLED showed excellent performance, with \( \text{CE}_{\text{max}}, \text{PE}_{\text{max}}, \text{and EQE}_{\text{max}} \) of 19.1\%, 33.5 cd A\(^{-1}\) and 23.9\%, respectively. In the solution-processed OLED the \( \lambda_{EL} \) was 556 nm. The device performance was somewhat lower but still excellent, especially in the context of solution-processed device [ITO/PEDOT:PSS, 35 nm/5 wt% QAO-DAd:CBP (20 nm)/TmPyPB (50 nm)/Liq (2 nm)/Al (120 nm)] performance, with \( \text{CE}_{\text{max}}, \text{PE}_{\text{max}}, \text{and EQE}_{\text{max}} \) of 68.2 cd A\(^{-1}\), 51.1 lm W\(^{-1}\), and 19.3\% respectively).

Zhang and co-workers reported phenyl-substituted analogs of QAO, known as 3-PhQAD and 7-PhQAD.[82] These two isomers differ only in the regiochemistry of the phenyl substituent (Figure 17). The two isomers were synthesized in an analogous procedure to Jiang and co-workers,[80] with 3-PhQAD and 7-PhQAD obtained after chromatographic separation in 53\% and 27\% yield, respectively. For both emitters, DFT calculations suggest that the additional phenyl ring modulates only to the distribution of the HOMO while the LUMO resides on the fused core. The calculated reorganization energies of 0.22 and 0.08 eV for 3-PhQAD and 7-PhQAD, respectively, which showed that 7-PhQAD would have a narrower emission spectrum compared to 3-PhQAD isomer. Sharp emission bands and a very small Stokes shifts in toluene solutions were observed, which are hallmarks of MR-TADF emitters. In toluene, both compounds showed narrow, blue emission similar to that of QOA core; for 3-PhQAD (\( \lambda_{PL} = 466 \) nm, FWHM = 30 nm) and 7-PhQAD (\( \lambda_{PL} = 464 \) nm, FWHM = 22 nm). There is only a small degree of positive solvatochromism, which the authors contend is evidence of an emissive excited state with mixed LE and CT character (vide infra). The \( \Delta E_{CT} \) values in 2 wt\% mCP film are 0.18 and 0.19 eV for 3-PhQAD and 7-PhQAD, respectively, which translated in a long \( \tau \) of 250 and 474 \( \mu \)s, respectively, which is much higher than the parent core (QOA) and the DABNA series. The device stack used in this report was ITO/TAPC, 35 nm/TCTA, 10 nm/2 wt% dopant in mCP, 20 nm/TmPyPB, 40 nm/LiF, and 1 nm/Al. The OLEDs with both emitters showed similar efficiencies compared to the device employing the parent QAO as the emitter. The 3-PhQAD-based OLED exhibited a \( \lambda_{EL} \) of 480 nm (FWHM = 44 nm) with CIE coordinates of (0.13, 0.32), while the 7-PhQAD-based OLED showed a narrower and blueshifted \( \lambda_{EL} \) of 472 nm (FWHM = 34 nm) and CIE coordinates of (0.12, 0.24). The maximum EQE, CE and PE observed for the device with 7-PhQAD are 18.7\%, 28.8 cd A\(^{-1}\) and 28.2 lm W\(^{-1}\), similar to the device with QOA, while the device with 3-PhQAD exhibited maximum EQE, CE and PE of 19.1\%, 33.5 cd A\(^{-1}\) and 32.9 lm W\(^{-1}\). The maximum brightness of the devices that were reached with these emitters were 4975 and 2944 cd m\(^{-2}\), respectively, for 3-PhQAD and 7-PhQAD based devices. Both devices, however, suffered from serious efficiency roll-off, which was identified to originate from a triplet-triplet annihilation (TTA) channel at low driving voltage based on theoretical stimulations, while at higher driving voltage singlet exciton–polaron annihilation (SPA) and TTA process contributes to the exciton loss channels in the device.

Recently we reported[61] a derivative of QAO/QAD (a.k.a. DiKTa; Figure 18)[60] Most of the MR-TADF emitters reported involved very low doping, often no more than 1 wt\% in film. This was necessary to prevent aggregation-caused quenching (ACQ), which are expectedly large for such planar molecules. In order to mitigate ACQ we developed the mesitylated derivative, Mes\(_3\)DiKTa. Spin-component scaling second-order approximate Coupled-cluster (SCS-CC2) calculations confirmed that both compounds are MR-TADF, with \( \Delta E_{CT} \) of 0.27 and 0.26 eV for DiKTa and Mes\(_3\)DiKTa, respectively. The synthetic route of DiKTa followed the previously reported protocol.[51,63] Direct bromination of DiKTa was not possible, but bromination in high yield of 84% was possible on the diester. Friedel–Crafts acylation produced Br\(_3\)DiKTa, which was elaborated to install the mesityl groups by Suzuki–Miyaura coupling to afford Mes\(_3\)DiKTa. Single crystal analysis showed different packing
structures with π–π interactions disrupted in the Mes3DiKTa crystal. The modified emitter presented reversible oxidation and reduction waves in the cyclic voltammograms, which is due to the inhibition of electrochemical degradation processes located at the para positions to that of central nitrogen. Moderate positive solvatochromism of ≈31 nm for both is observed, consistent with a short-range charge transfer. A modest redshift in the emission from DiKTa (453 nm) to Mes3DiKTa (468 nm) in toluene was also noted, which was the result of the inductively electron-withdrawing nature of the mesityl groups that stabilize the LUMO resulting in a reduced band gap. In addition, the modified emitter presented a slightly shorter lifetime of 23 µs in toluene compared to the parent (33 µs). ACQ was strongly suppressed in mCP films of Mes3DiKTa. Further, in neat DiKTa films two emission peaks at 475 and 536 nm were observed, the latter of which we attributed to excimer formation. This lower energy emission was not observed in neat films of Mes3DiKTa. In 3.5 wt% emitter in mCP, ∆E_ST was calculated to be 0.20 and 0.21 eV for DiKTa and Mes3DiKTa, respectively. Devices were fabricated in the configuration ITO/HAT-CN, 10 nm/TAPC, 40 nm/TCTA, 10 nm/3.5 wt% emitter:mCP, 20 nm/TmPyPb, 50 nm/LiF, 1 nm/Al, 100 nm. Both the device shown a low turn on voltage of 3 V. The OLED with Mes3DiKTa showed an EQE_max of 21.2%, (25 cd m⁻²) which was superior to the device with DiKTa at 14.7% (8 cd m⁻²). Improved efficiency roll-off was observed for the device with Mes3DiKTa where there was only 31% roll-off at 100 cd m⁻² compared to 44% for the OLED with DiKTa. Both DiKTa and Mes3DiKTa displayed higher brightness than previously reported ketone MR-TADF emitters including that reported with the QOA emitter, with maximum luminance values of 10 385 and 12 949 cd m⁻², respectively. These luminances compare favorably to that reported for 3-PhQAD at 4795 cd m⁻². Similar to the trends in the solution-state photophysics, a 15 nm redshift in the electroluminescence spectrum was observed for the OLED with Mes3DiKTa to that of DiKTa, from CIE (0.14,0.18) to (0.12,0.32).

### 3. Modeling of MR-TADF Emitters

DFT is the standard computational approach for the investigation of the optoelectronic properties of TADF (and indeed all) emitters. It has been widely, and often wisely, used to rationalize molecular design and provide greater insight into the TADF mechanism. Conventional hybrid functionals, particularly B3LYP,[64] PBE0 [65] and range-corrected functionals including omega-tuned LC_PBE[66] have emerged as the most popular in the TADF literature. For D–A TADF emitters, these methods usually offer good quantitative agreement with experiment for both ∆E_ST and S₁ energies and qualitative agreement with experiment for spectral linewidths as inferred from calculated

| Compound | Method used in the literature | ∆E_ST [CALC] (Eₐ) calculated in the literature [eV] | ∆E_ST [EXPL] [eV] | ∆E_ST [CALC] SCS[61] [eV] | Ref. |
|----------|-------------------------------|---------------------------------------------------|------------------|---------------------------|-----|
| 2a       | TD-B3LYP/6-31g(d)             | N/A (0.52)                                        | 0.15             | 0.20                      | [28]|
| DABNA-1  | TD-B3LYP/6-31g(d)             | 0.49 (0.39)                                       | 0.18             | 0.16                      | [27a]|
| DABNA-2  | TD-B3LYP/6-31g(d)             | 0.42 (0.30)                                       | 0.14             | 0.14                      | [27a]|
| 2α       | TD-B3LYP/6-311g(d,p)          | N/A                                               | 0.21             | 0.17                      | [33]|
| TBN-TPA  | TD-B3LYP/6-31g(d)             | N/A                                               | 0.14             | 0.13                      | [36]|
| r-DABNA  | N/A                           | N/A                                               | 0.14             | 0.13                      | [38]|
| QAO      | TD-B3LYP/6-31g(d)             | N/A                                               | 0.17             | 0.15                      | [60]|
| 3-Ph-QAD | TD-B3LYP/6-31g(d)             | 0.60                                              | 0.18             | 0.27                      | [62]|
| 7-Ph-QAD | TD-B3LYP/6-31g(d)             | 0.55                                              | 0.19             | 0.27                      | [62]|

Table 3. Literature-obtained values of TD-DFT calculated and experimentally determined ∆E_ST values for all MR-TADF emitters reported to date, and calculations performed by us using SCS-CC2 (excitations are vertical absorption unless stated as adiabatic energy (Eₐ)).
relaxation energies. Unfortunately, DFT predictions fall apart for MR-TADF emitters, especially in terms of predicted $\Delta E_{ST}$ values, often consistently overestimated; notably, and in a way very symptomatic, most reports to date only discuss ground-state DFT calculations, with time-dependent DFT results more rarely presented (Table 3). In order to tackle the modeling of this class of emitters, several theory papers have emerged. The excited-state dynamics of DABNA-1 and DABNA-2 were investigated\(^{67}\) to rationalize why DABNA-2 shows an enhanced $\Phi_{PL}$ in the film compared to solution, while for DABNA-1 there is little change in the $\Phi_{PL}$\(^{27a}\). Differing nonradiative decay processes were proposed for the two emitters.\(^{67}\) In DABNA-2 nonradiative decay is dominated by low frequency twisting of the pendant phenyl groups, which would be significantly suppressed in the solid state. In DABNA-1 the C–C stretching is the primary source of nonradiative decay. As these stretching modes are high-frequency processes there would be no significant difference between solution and film. Large $\Delta E_{ST}$ values of 0.33 eV were predicted for both compounds, which significantly overestimate the experimentally determined values; DFT calculations do predict the presence of two intermediate triplet states sandwiched between $T_1$ and $S_0$. Although the authors contend that ISC takes place mainly between $S_1$ and $T_2$ due to their strongly coupled nature, the primary route for RISC was proposed to be $T_1$ to $S_1$. This proposed mechanism differs from the one postulated by Northey and Penfold,\(^{67}\) who propose that $T_2$ to $S_1$ is the primary route of RISC for DABNA-1, with almost no contribution from $T_1$. Quantum dynamics calculations of the $T_1$ and $T_2$ populations were applied to justify this mechanism, and $k_{RISC}$ was compared to experimentally derived values. There was poor agreement when considering only 1 singlet state within the model; however, when higher-lying singlet states were incorporated, the predictions became more accurate. The coupling between $S_1$ and higher energy singlet states helped improve spin–orbit coupling, which was mediated via vibronic coupling occurring within the molecule. Because RISC is facilitated by vibronic coupling between singlet states, the rigid nature of this emitter implies a slower $k_{RISC}$ than exists in conventional D–A TADF emitters, which have more conformational freedom. Although the modeling does accurately model the RISC kinetics, again $\Delta E_{ST}$ was poorly predicted, with a value of 0.59 eV being reported.\(^{67b}\) When the functional MPWK1CIS was used to model DABNA-1 and DABNA-2, good agreement between $\Delta E_{ST,EX} (0.18$ eV) and $\Delta E_{ST,CALC} (0.21$ eV) was obtained.\(^{68}\) No explanation was provided as to why this approach worked so well. This methodology was used to predict $\Delta E_{ST}$ and $k_{nr}$ for both DABNA-1 and DABNA-2, and for a series of functionalized derivatives incorporating additional donor moieties to the DABNA-1 core.

We recently reported a much-improved computational protocol to model MR-TADF compounds, moving away from DFT and using instead a wave function-based approach, SCS-CCZ.\(^{49}\) Excellent agreement was achieved for the $\Delta E_{ST}$ values of both DABNA-1 and 2a (Figure 4) and a proposed design of new extended derivatives offered a tantalizing path to generate molecules showing both decreasing $\Delta E_{ST}$ and increasing oscillator strength. The success of this method is ascribed to the inclusion of second-order contributions to the excitations energy that include to some extent double excitations which offer in comparison to TD-DFT a better treatment of both the dynamic and the static electron correlation leading to a better estimate of the $S_1$ energy. Overall, the poor description in TD-DFT with the conventional functional (hybrid and range-separated) of the $S_1$ excited state inherently results in an overestimated $\Delta E_{ST}$ for the MR-TADF emitters (Figure 19).\(^{49,63}\) This work also offered a design strategy to simultaneously reduce $\Delta E_{ST}$ and increase oscillator strength, which is not possible for D–A TADF emitters (Figure 19d). Extension of the DABNA core produced compounds that had reduced $\Delta E_{ST}$ from 0.17 eV in 3 to 0.003 eV in 6, accompanied by increased oscillator strength for the $S_0$–$S_1$ transition from 0.23 to 1.07; increasing the conjugation in these DABNA derivatives also resulted in a predicted redshift in the emission due to the increase in excited state wavefunction delocalization. Further tuning of the emission wavelength can be achieved, for instance by introducing additional N- or B-atoms into the compound. For the sake of illustration, we designed two other molecules, 7 and 8, based on 5. These chromophores essentially retain the properties of the parent molecule in terms of $\Delta E_{ST}$ and oscillator strength but with tuned emission, blueshifted to 2.85 eV (435 nm, deep blue, 7) and redshifted to 2.1 eV (590 nm, yellow, 8) compared to 5. Up to now, color tuning has proven difficult with the current cohort of MR-TADF emitters covering only 100 nm range, spanning deep blue to sky blue. Although the prospect of efficient blue devices is desirable, the concept of a rigid TADF red emitter mitigating $k_{nr}$ is underexplored yet seemingly possible with our design.

4. Conclusions and Outlook

OLEDs using purely organic D–A TADF compounds have achieved comparable, and for some colors even surpassed, performance metrics compared to state-of-the-art OLEDs employing organometallic phosphorescent complexes.\(^{17}\) Color purity remains an issue, particularly for blue-emitting devices, and this can best be addressed with narrow-band emitters. MR-TADF emitters in this regard distinguish themselves from D–A TADF emitters, and provide a potential, and long-sought after, solution for high efficiency pure blue OLEDs. Efficiency roll-off remains an issue to be adequately addressed for MR-TADF-based OLEDs, with poor roll-off for most emitters, and device stability is yet to be optimized. However, despite the small number of structurally related examples reported, it is already evident that MR-TADF emitters are an incredibly promising class of compounds. Especially through the report of ν-DABNA from Hatakeyama and co-workers\(^{25b}\) MR-TADF compounds have set high standards as pure blue TADF emitters. The device with ν-DABNA exhibited pure blue emission (CIE = 0.12, 0.11) due in part to its very narrow emission band (FWHM = 18 nm) and showed a remarkable $\text{EQE}_{\text{max}}$ of 34.4%, which fell only to 26% at 1000 cd m$^{-2}$. The FWHM of this device is the same as that of the best micro LED device\(^{69}\) and smaller than that reported from a high-performance QD-LED device.\(^{70}\) It remains to be seen whether high-performance MR-TADF emitters can be developed in the pure green and red regions of the visible spectrum. Devices reported by Duan and co-workers\(^{48}\) demonstrated an impressive CIE of 0.60, indicates the potential of MR-TADF emitters to address colors other than blue in
OLEDs. A more complete understanding of the design rules for developing MR-TADF emitters is required, as is an exploration of a wider chemical space beyond triangulene-type compounds. Most of the MR-TADF emitters are reported to have very small delayed contributions to the radiative decay process, which is likely the result of the moderate $\Delta E_{ST}$ values that are sufficiently small to turn on TADF nevertheless govern an inefficient RISC process. On a more fundamental level, additional study is required to strengthen an understanding of the excited-state behavior of this class of compounds, including how to modulate emission color, $\Delta E_{ST}$ and $k_{RISC}$. The importance of intermediate triplet states, identified as important in efficient D–A TADF emitters, has not been systematically considered in MR-TADF compounds. Finally, it is only recently that an adequate computational model has been developed. With this in hand in silico design of new MR-TADF emitters becomes feasible, which should lead to an acceleration of materials discovery.

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Conflict of Interest

The authors declare no conflict of interest.

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