The 1,3,5-triazine electron acceptor has become one of the most popular building blocks for the design of thermally activated delayed fluorescence (TADF) materials. Many TADF design strategies are first applied in compounds that contain triazines, and there are numerous examples of organic light-emitting diodes (OLEDs) with triazine-containing emitters that show high efficiencies and long operating lifetimes. A comprehensive review of triazine-containing TADF emitters is provided. This review is organized according to the triazine-derived structural motifs, such as number and position of electron-donor groups in donor–acceptor-type emitters, the π-bridging linkers employed, orientation control of the transition dipole moment, and the design of chiral and through-space charge-transfer emitters. The structure of the compounds with their optoelectronic properties and the corresponding performance of the OLED devices is correlated.

1. Introduction

Since 1987, when the first viable electroluminescent device was reported by Tang and Van Slyke,[1] significant progress has been made in terms of materials development such that organic light-emitting diodes (OLEDs) have now been commercialized in both the solid-state lighting and display markets. The current mature OLED products heavily rely on the phosphorescent emitters that contain noble metals such as iridium because these materials permit 100% utilization of the electrogenerated singlet and triplet excitons to produce light. The breakthrough of TADF materials in 2012 by Adachi and co-workers[2] provides an alternative route to reach equally efficient OLEDs and without the use of these scarce metals. To date, thousands of TADF materials have been reported, and their use in red, green, and blue OLEDs has been demonstrated. Importantly, there are now many examples of devices that show high external quantum efficiency (EQE), device stability, and color purity; these reports demonstrate that TADF OLEDs are attractive alternatives to phosphorescent devices. Indeed, the first commercialized TADF OLED devices are now on the market.[3] For instance, one of the best red TADF OLED, which uses TPA-PZCN as the emitter, has realized a record high maximum EQE (E_{EQEmax}) of 28.1% with an electroluminescence maximum, \( \lambda_{EL} \), of 648 nm.[4] For green OLEDs, the use of CzDBA as the emitter resulted in a device with an E_{EQEmax} of 37.8% with the \( \lambda_{EL} \) at 528 nm.[5] Blue OLED employing TDBA–D1 as the emitter showed a comparable high E_{EQEmax} of 38.2% with CIE coordinates of (0.15, 0.28)[6] and an OLED using a multiple resonance TADF (MR-TADF) emitter, \( \nu \)-DABNA, achieved an E_{EQEmax} of 34.4% with a \( \lambda_{EL} \) at 469 nm and a full-width at half-maximum (FWHM) of only 18 nm.[7]

All these achievements in terms of device performance are inextricably linked to the development of high-performance highly twisted donor–acceptor emitter architectures. The vast majority of electron-donor groups used within TADF emitters are hole-transporting N-heterocycles and are typically chosen from carbazole and its derivatives (e.g., bcarbazole, benzofuro-carbazole, thiencarbazole, and indolocarbazole), aryamine, acridan, phenoxazine, phenothiazine, and phenazine, and their derivatives. There is more structural diversity in the electron-acceptor moiety, with popular motifs containing borane, sulfone, ketone, pyrimidine, benzonitrile, thiphthalonitrile, triazole, oxadiazole, thiadiazole, benzothiazole, benzooxazole, quinoxaline, anthraquinone, heptazine, and, of course, triazine. In particular, 1,3,5-triazine has been one of the most popular electron-deficient heteroaromatic acceptors used in green and blue TADF emitters and is also a popular component used in host materials design due to its moderate electron affinity with the LUMO values in the range of \(-2.7\) to \(3.1\) eV.[8] Most commonly, the 1,3,5-triazine is decorated by three phenyl groups attached to the 2,4,6-position of triazine in a triphenyltriazine structure (TRZ). There are also examples of triazine-containing materials where the electron donor is directly attached to the triazine. However, in many of these materials, as there are negligible steric interactions between the triazine and the donor, thus leading to a predominantly coplanar conformation, there is significant overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), thereby resulting in a correspondingly large singlet and triplet energy splitting (\( \Delta E_{ST} \)) and no TADF. For example, DPhCzT,[9] a compound
containing a carbazole directly coupled to a diphenyltriazine, was reported as a host material, but did not show any TADF properties due to its large $\Delta E_{ST}$ of 0.3 eV (Figure 1).

The genesis of organic TADF materials as emitters for OLEDs was in 2011 and relied on a triazine-based compound (Figure 2). A sufficient separation between HOMO and LUMO was induced by strengthening the electron donor by extending the conjugation length as was done in PIC-TRZ ($\Delta E_{ST} = 0.11$ eV), the first example of a purely organic TADF emitter. The design of PIC-TRZ also paved the way for the adoption of one of the most successful design strategies for TADF emitters, which is based on a strongly twisted donor-$\pi$-acceptor motif. Exciplex systems are another route to small $\Delta E_{ST}$ as the weak intermolecular interactions between electron-donor and electron-acceptor compounds ensure suitable physical separation of the HOMO and LUMO. Triazine-containing electron acceptors appear prominently in exciplex systems due to their largely planar conformation since the first exciplex system was reported in 2012.\textsuperscript{[10]} PO-T2T, for instance, has
been widely used as the acceptor for exciplex since it was first reported in 2014.\textsuperscript{[11]} Triazine electron acceptors were incorporated into some of the first TADF dendrimer emitters in 2015, such as G3TAZ, this due in part to the D_2-symmetric structure of the TRZ and the ease with which chemical modification of this core can occur. High-efficiency nondoped OLEDs (EQEmax = 20%) using the small molecule emitter DMAC-TRZ showed comparable performance to the doped device, indicating that it is possible to design a compound that shows significantly suppressed concentration quenching in neat films. DMAC-TRZ is still one of the most widely studied donor–acceptor-type TADF emitters. Disposing the electron-donor adjacent to the TRZ results in improved performance in the OLED, as exemplified by TRZ-oCz (EQEmax = 9.3%). This is partially due to the more strongly twisted conformation that must be adopted for this compound and the additional through space charge transfer (TSCT) state that is induced. Since the first example in 2017, TRZ-containing TSCT TADF emitters have developed rapidly. Presently, the highest performing TRZ-based TADF emitter is SpiroAC-TRZ. Compared to the OLED with DMAC-TRZ, the EQEmax of the OLED with SpiroAC-TRZ is improved to 36.7%. Here, by employing a related electron donor in 10H-spiro [acridine-9,9’-fluorene] (SpiroAC), a highly horizontally orientated transition dipole moment (TDM) was achieved, leading to enhanced light outcoupling.\textsuperscript{[12]} Recently, a triazine-containing TADF emitter 5Cz-TRZ with five carbazoles closely packed onto a central phenylene bridge afforded a material with one of the fastest reverse intersystem crossing (RISC) rate constants of kRISC = 1.5 × 10^7 s\(^{-1}\).

There are several advantages for the use of triazine within TADF materials. These include (1) triazine and its derivatives are easy to synthesize from inexpensive starting materials; (2) triazine is easily functionalized at the 2,4,6 positions and can be done both symmetrically or asymmetrically, thereby increasing structural diversity; (3) the linkage between the electron donor and the triazine core can be rationally adjusted; and (4) triazine is a stable aromatic structure that contributes to improved operational lifetimes of the devices. Documenting the popularity of this moiety, in this review, we summarize the recent progress of triazine-containing TADF materials. First, the TADF emitters based on carbazole-triazine structures are introduced and classified according to 1) the number and substitution position of the carbazole; 2) the influence of the bridge between the donor and the triazine acceptor; 3) the influence of the structure on the orientation of the emitter within the emitter layer, which will affect the orientation of the TDM and hence the light outcoupling efficiency in the device; 4) trisubstitution about the triazine core; 5) dimerization strategies where there are at least two triazines within the material; 6) examples where the linker group goes beyond a phenylene; 7) adjustment of the triazine electron-withdrawing strength through peripheral decoration; and 8) examples where there is TSCT in addition to through-bond charge transfer (TBCT). Finally, moving beyond carbazole-based electron donors, examples of emitters using other donors will be summarized (Figure 3).

2. Influence of Carbazole (Number and Position) on the Properties of TRZ-Based TADF Emitters

Carbazole (Cz) has been widely used as an electron-donating group in optoelectronic materials because of its moderate donor strength and the ease with which chemical derivatization can occur.\textsuperscript{[13]} Carbazole is also a fully aromatic structure, with no bonds to a sp\(^3\)-centre as exists in acridine, phenoxazine, and phenothiazine, bonds that are prone to scission and routes to degradation in the device.

First, we compare the optoelectronic properties of Cz-TRZ derivatives where the Cz is either ortho, meta or para disposed with respect to the diphenyltriazine, as shown in Figure 4. The para-analog CzTRZ (here, it is renamed as p-CzTRZ), first reported by Lee et al.,\textsuperscript{[14]} is not a TADF emitter due to its too strong conjugation between Cz and TRZ, leading to a large ΔE_{ST} of 0.36 eV; the compound is a blue emitter with a λPL of 449 nm and a photoluminescence quantum yield, ΦPL, of 71% (10 wt% DPEPO). A blue OLED with CIE coordinates of (0.17, 0.11) showed only an EQEmax of 4.2%. A slightly improved OLED efficiency (EQEmax of 5.8%) was later reported by our group,\textsuperscript{[15]} which provided further confirmation that in the device p-CzTRZ acts as a fluorescent emitter. Liao et al.\textsuperscript{[16]} designed two analogs, SFCCN and SFCCNO (Figure 5), based on the strategy of introducing a secondary donor group onto the carbazole moiety of p-CzTRZ. The solution-state properties remained unchanged because the spiro-carbon linkage between the secondary donor with carbazole is not conjugated. However, in the neat films, the aggregation of these molecules triggered the TADF as a result of the intermolecular TSCT. The planar molecular conformation is believed to facilitate face-to-face
intermolecular interactions required for the TSCT to occur. The nondoped device based on SFCCNO exhibited an EQE of 12.9% at 100 cd m$^{-2}$, which is much improved compared to the device based on the non-TADF emitter $p$-CzTRZ (1.5% at 100 cd m$^{-2}$).

The meta- and ortho- analogs, by contrast, are efficient TADF emitters. CzTRZ (renamed as o-CzTRZ; $\lambda_{PL} = 455$ nm, $\tau_d = 3.90$ µs in 5 wt% mCP film) possesses a much smaller overlap between the HOMO and LUMO as a result of the more strongly twisted conformation ($87.3^\circ$ for the dihedral angle between carbazole and phenylene bridge determined from the crystal structure[17]), which translates into a compound with a $\Delta E_{ST}$ of 0.1 eV in 5 wt% mCP film. By doping 5 wt% o-CzTRZ in mCP host as the emitting layer, the OLED exhibited a blue emission with a $\lambda_{EL}$ at 470 nm and an EQE$_{max}$ of 9.3% despite the $\Phi_{PL}$ of o-CzTRZ being only 16.7% (5 wt% mCP), which likely implies that the $\Phi_{PL}$ has been underestimated, considering the

Figure 4. Molecular structures and properties of TADF emitters containing carbazole-triazine motifs.
device performance. Interestingly, the full-width at half-maximum (FWHM) of the blue TADF device is only 66 nm, which we attribute to a much reduced geometric reorganization in the excited state to the small degree of conformational freedom present in the ortho-linked system. Indeed, many other compounds containing ortho-linked donors and acceptors also show narrow emission spectra (in section 9 related to TSCT). Normally, meta-disposed electron donors and electron acceptors in D–A-type emitters show the weakest conjugation compared to their ortho- and para-analogs, which should lead to a correspondingly smaller $\Delta E_{ST}$. However, it was observed by Wu et al.\textsuperscript{[19]} that the $\Delta E_{ST}$ of \textit{m-CzTRZ} (0.22 eV in 10 wt\% in mCP film) is indeed larger than 0.03 eV for \textit{o-CzTRZ} (determined again by Wu et al.\textsuperscript{[19]} although these values are extracted from the energy difference between the PL at room temperature and the phosphorescence spectra at 77 K in 2-MeTHF and so differ from those of Gong et al.\textsuperscript{[17]})\textsuperscript{,}5\textsuperscript{,}17\textsuperscript{a} The authors contended that the smaller observed $\Delta E_{ST}$ for \textit{o-CzTRZ} resulted from the near orthogonal conformation of the donor, leading to near complete suppression of the conjugation between Cz and TRZ. The DFT calculations (Figure 6) from their work suggest that the $^1$LE state of \textit{m-CzTRZ} is much more stabilized than the $^1$CT state, while the $^1$LE state of \textit{o-CzTRZ} is much closer in energy to its $^1$CT state. The stabilized $^1$LE state explains the greater $\Delta E_{ST}$ of \textit{m-CzTRZ} than that of \textit{o-CzTRZ} due to their similar energy in $^1$CT state, resulting in calculated $\Delta E_{ST}$ of 0.06 eV and 0.23 eV for \textit{o-CzTRZ} and \textit{m-CzTRZ}, respectively, which are consistent with the experimental values. The OLEDs exhibited high EQE\textsubscript{max} of 17.5\% and 19.2\% for the devices with \textit{o-CzTRZ} and \textit{m-CzTRZ}, respectively (10 wt\% doped in mCP host). Further, the EQE\textsubscript{max} of the corresponding nondoped OLEDs remains nearly as high at 17.6\% and 16.7\% for the devices with \textit{o-CzTRZ} and \textit{m-CzTRZ}, respectively.

In comparison to the three aforementioned triazine-based TADF emitters, each possessing only one carbazole donor, emitters with more than one carbazole have also been investigated. Lee et al.\textsuperscript{[20]} reported a stable deep blue emitter DCzTRZ ($\lambda_{PL}$: 459 nm; $\Phi_{PL}$: 43\% in toluene) in which the two carbazole donor groups are disposed mutually meta to each other and to the triazine acceptor. The $\Delta E_{ST}$ of DCzTRZ is 0.25 eV, which is similar to that of \textit{m-CzTRZ} (0.22 eV in 10 wt\% mCP). The blue OLED has an EQE\textsubscript{max} of 17.8\% at CIE coordinates of (0.15, 0.15), which is slightly less efficient than that of \textit{m-CzTRZ} (19.2\%). It is surprising to observe a much bluer emission spectrum in comparison with the device based on \textit{m-CzTRZ}, although the solution PL spectrum in toluene is exactly the same. The bluer-shift of the EL may be caused by the different device configurations, choice of host, and doping concentration between the two devices.

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**Figure 5.** Molecular structures of SFCCN and SFCCNO.

**Figure 6.** HOMO and LUMO distribution and their energy levels, optimized $S_1$ geometry with oscillator strengths ($f$) for \textit{o-CzTRZ} and \textit{m-CzTRZ}. Reproduced with permission.\textsuperscript{[19]} Copyright 2019, Royal Society of Chemistry.
A number of other analogs containing two carbazole donors were also prepared by Lee et al.\cite{21} The different substitution patterns of the two carbazoles for six emitters 23CT, 24CT, 25CT, 26CT, 34CT, and 35CT (here DCzTRZ was renamed as 35CT) are correlated with their photophysical properties. Ortho-substitution to the triazine acceptor induces a large dihedral angle between the carbazole and triazine moieties, thus leading to a stronger charge transfer state and smaller $\Delta E_{\text{ST}}$, which is evident by comparing 23CT ($\Delta E_{\text{ST}}$: $-$0.02 eV, 1 wt% in Zeonex), 24CT ($\Delta E_{\text{ST}}$: 0.11 eV, 1 wt% in Zeonex), 25CT ($\Delta E_{\text{ST}}$: 0.07, 1 wt% in Zeonex), and 26CT ($\Delta E_{\text{ST}}$: $-$0.07 eV, 1 wt% in Zeonex) with 34CT ($\Delta E_{\text{ST}}$: 0.29 eV, 1 wt% in Zeonex) and 35CT ($\Delta E_{\text{ST}}$: 0.24 eV, 1 wt% in Zeonex). The difference of $\Delta E_{\text{ST}}$ may result from different conformers, showing the various CT strength. The emitters with no ortho-substituted carbazole have larger $\Delta E_{\text{ST}}$ and long-to-negligible delayed fluorescence. The EQE$_{\text{max}}$ of the OLEDs with 23CT, 24CT, and 34CT as emitters are 21.8%, 22.4%, and 13.3%, respectively, which align with both the smaller $\Delta E_{\text{ST}}$ and faster RISC rates of the former two emitters.

There are also a number of analog emitters possessing three carbazole donors. Compared with 35CT ($\Delta E_{\text{ST}}$: 0.23 eV; $\Phi_{\text{PL}}$: 43% in toluene), TCzTRZ\cite{22} ($\Delta E_{\text{ST}}$: 0.16 eV; $\Phi_{\text{PL}}$: 100% in toluene), as shown in Figure 7, possesses a smaller $\Delta E_{\text{ST}}$ coupled with a significantly improved $\Phi_{\text{PL}}$. The structural difference between these two compounds is the addition of a third carbazole para to the triazine, which results in a HOMO that is distributed over the three donor carbazoles. The even distribution of the electron density of the HOMO across multiple donors also is in operation in TmCzTRZ ($\Delta E_{\text{ST}}$: 0.07 eV; $\Phi_{\text{PL}}$: 99% in toluene), which also possesses a smaller $\Delta E_{\text{ST}}$ and a higher $\Phi_{\text{PL}}$ than DCzmCzTRZ ($\Delta E_{\text{ST}}$: 0.20 eV; $\Phi_{\text{PL}}$: 84% in toluene), which has two different carbazole-based donors. OLEDs with these three emitters achieved comparably high efficiencies, with EQE$_{\text{max}}$ of 25% and CIE coordinates of (0.18, 0.33) for the device with TCzTRZ and an EQE$_{\text{max}}$ of 25.5% and CIE coordinates of (0.25, 0.50) for the device with TmCzTRZ; the red-shift in the EL of the latter is due to the use of a stronger dimethylcarbazole donor. The EQE$_{\text{max}}$ decreased to 21.3%, with CIE coordinates of (0.23, 0.46) for the device with DCzmCzTRZ, reflecting to the lower $\Phi_{\text{PL}}$ for the emitter.

Lee et al.\cite{23} later probed the effect of the regiochemistry of the three carbazole donors on the photophysical properties of the emitters. A cross-comparison of the photophysical properties of compounds 234CzTRZ ($\Delta E_{\text{ST}}$: 0.07 eV; $\Phi_{\text{PL}}$: 90% in DPEPO; $\tau_{\text{d}}$: 4.1 $\mu$s), 235CzTRZ ($\Delta E_{\text{ST}}$: 0.14 eV; $\Phi_{\text{PL}}$: 100% in DPEPO; $\tau_{\text{d}}$: 8.4 $\mu$s), and 245CzTRZ ($\Delta E_{\text{ST}}$: 0.17 eV; $\Phi_{\text{PL}}$: 98.4% in DPEPO; $\tau_{\text{d}}$: 9.7 $\mu$s) revealed that the substitution pattern of the three carbazole donors affects both $\Delta E_{\text{ST}}$ and $\tau_{\text{d}}$; all three compounds possess a shorter delayed fluorescence lifetime than that of TCzTRZ ($\tau_{\text{d}}$: 13.5 $\mu$s). As shown in Figure 8, the ortho-substituted carbazoles to the diphenyltriazine acceptor adopt a large dihedral angle, which leads to a shortened delayed fluorescence lifetime, compound 234CzTRZ, with three

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Figure 7. Molecular structures and properties of TADF emitters containing three carbazole donors and a triazine acceptor.
carbazoles packed closely to each other, showed the shortest delayed lifetime of 4.1 μs. The EQEmax of the OLEDs using 234CzTRZ (λEL: 497 nm; CIE = (0.20, 0.44)), 235CzTRZ (λEL: 495 nm; CIE = (0.20, 0.45)), and 245CzTRZ (λEL: 490 nm; CIE = (0.17, 0.39)) are all quite similar at 20.4%, 18.7%, and 22.0%, respectively. At a luminance of 1000 cd m⁻², the device with 234CzTRZ can still maintain 18.4%, while the EQE₁₀₀₀ of the OLEDs with 235CzTRZ and 245CzTRZ drops to 14.7% and 13.8%, respectively. However, even though these emitters exhibited shorter τDF and smaller ΔE_ST than those of TCzTRZ, their devices' performance is inferior to the OLED based on TCzTRZ.

Recently, a TADF emitter 5Cz-TRZ (ΔE_ST: 0.06; Φ.PL: 99% (15 wt% mCBP); τ_DF: 0.8 μs in DMF) was the first reported purely organic TADF emitter for use in OLEDs (Figure 2). Unlike the most commonly used design strategy for TADF emitters, which is to separate electron-donor and electron-acceptor groups by a conjugated phenylene bridge, 5Cz-TRZ contains two carbazole derivatives that are directly connected to a triazine core. A relatively small ΔE_ST (0.11 eV) was obtained due to the large twist angle between the carbazole-based donors and the triazine acceptor. Even though the reported EQEmax could only reach 5.3% for the sky-blue OLED, this nevertheless indicated that upconversion of triplet excitons to singlet excitons was occurring as the theoretical EQEmax of the device was limited to 2% based on its relatively low Φ.PL of 39% and assuming no triplet exciton harvesting (Figure 10).

Figure 8. Results of molecular orbital calculations showing frontier molecular orbitals distribution and geometry of 234CzTRZ, 235CzTRZ, and 245CzTRZ. Reproduced with permission.© 2019, Wiley-VCH.
Figure 9. a) EQE versus luminance characteristics. b) Normalized EL spectra. c) Transient EL decay characteristics of devices A, B, and C at 10, 1000, and 5000 cd m\(^{-2}\), a.u., arbitrary units. d) Operational lifetimes of the TADF and hyperfluorescent OLEDs. Reproduced with permission.[24] Copyright 2020, Nature Portfolio.

Table 1. Summary of photophysical and electrochemical properties.

| Emitter | Solution \(\lambda_{PL}/\Phi_{PL}/\tau_{PL}\) (medium) | Solid State \(\lambda_{PL}/\Phi_{PL}/\tau_{PL}\) (medium) | \(\Delta E_{CT}\) | HOMO | LUMO | Ref. |
|---------|-----------------------------------------------------|-----------------------------------------------------|-----------------|--------|--------|------|
| CzTrz  | / / /                                              | / / / (10 wt% in DPEPO)                            | 0.36            | -6.04  | -3.39  | [14] |
| m-CzTrz | 431 / / (PhMe)                                    | \approx 425 / / -6.44 (10 wt% in mCP)              | 0.22            | -5.62  | -2.77  | [19] |
| o-CzTrZ | / / /                                            | 455 / / -3.9 (5 wt% in mCP)                        | 0.10            | -6.12  | -3.26  | [17] |
| 26CT   | \approx 465 / / (PhMe)                             | / / /16.4 ± 0.9 (1% wt in ZEONEX)                 | -0.07           | -     | -     | [21] |
| 25CT   | / / / (PhMe)                                      | / / /8.0 ± 1.2 (1% wt in ZEONEX)                   | 0.07            | -     | -     | [20] |
| DCzTrz | \approx 440/0.43 / (PhMe)                          | 429 / / -3.1 (polystyrene)                         | 0.25            | -5.88  | -2.86  | [21] |
| 23CT   | \approx 485 / / (PhMe)                             | / / /8.7 ± 0.3 (1 wt% in ZEONEX)                   | -0.02           | -6.12  | -3.52  | [21] |
| 24CT   | \approx 465 / / (PhMe)                             | / / /21.4 ± 1.9 (1% wt in ZEONEX)                  | 0.11            | -6.14  | -3.55  | [21] |
| 34CT   | \approx 450 / / (PhMe)                             | / / / (1% wt in ZEONEX)                            | 0.29            | -6.16  | -3.50  | [21] |
| TCzTrz | /100 (PhMe)                                       | \approx 460/100/13.5 (30 wt% in DPEPO)            | 0.16            | -     | -     | [22] |
| TrmCzTrz | / /99 (PhMe)                                     | \approx 475/100/13.3 (30 wt% in DPEPO)            | 0.07            | -     | -     | [22] |
| DCzmCzTrz | / /89 (PhMe)                                   | \approx 470/98/9.7 (30 wt% in DPEPO)              | 0.20            | -     | -     | [22] |
| 235CzTrz | \approx 480 / / (PhMe)                          | \approx 460/100/8.4                               | 0.14            | -     | -     | [23] |
| 245CzTrz | \approx 500 / / (PhMe)                         | \approx 450/98.4/9.7                               | 0.17            | -     | -     | [23] |
| 5Cz-TrZ | 486/92 / / (PhMe)                                 | 486/99/2.1 (15 wt% in mCBP)                        | 0.03            | -5.92  | -     | [24] |
Table 2. Summary of device structures and performance.

| Emitter | Device Structure | $\lambda_{EL}$ [nm] | CIE | $V_{on}$ [V] | EQE/PE/CE $100/1000$ $[\%/lm W^{-1}/cd A^{-1}]$ | EQE $100/1000$ $[cd m^{-2}]$ | Ref. |
|---------|-----------------|---------------------|-----|-------------|---------------------------------|-----------------|-----|
| CzTRZ   | ITO/PEDOT:PSS/TAPC/mCP/CzTrz/TSPO1/TBP/LiF/Al | 449 | (0.17, 0.11) | – | 4.2/2.7/3.8 | 1.5/0.6 | [14] |
| m-CzTRZ | ITO/PEDOT:PSS/TAPC/10 wt% m-CzTrz/mCP/TmPyPB/LiF/Al | $\approx$500 | (0.25, 0.44) | 3.3 | 19.2/40.3/51.3 | 15.7/N/A | [19] |
| α-CzTRZ | ITO/PEDOT:PSS/TAPC/mCP/5%CzTrz/TSPO1/LiF/Al | 470 | (0.15, 0.22) | – | 9.3/14.5 | – | – | [17] |
| DCzTRZ  | ITO/PEDOT:PSS/TAPC/mCP/25 wt% DCzTrz/DPEPO/TSPO1/TBP/LiF/Al | 459 | (0.15, 0.15) | 5.9 | 17.8/22.4/26.8 | 8.5/2.0 | [20] |
| 23CT    | ITO/PEDOT:PSS/TAPC/mCP/DPEPO:30 wt% 23CT/TSPO1/TPBi/LiF/Al | – | (0.17, 0.33) | – | 21.8/30.9/45.9 | 21.8/20.8 | [21] |
| 24CT    | ITO/PEDOT:PSS/TAPC/mCP/DPEPO:30 wt% 24CT/TSPO1/TPBi/LiF/Al | – | (0.15, 0.26) | – | 22.4/40.3/50.4 | 20.4/14.5 | [21] |
| 34CT    | ITO (120 nm)/PEDOT-PSS/TAPC/mCP/DPEPO:30 wt% 34CT/TSPO1/TPBi/LiF/Al | – | (0.15, 0.17) | – | 13.3/21.5 | 9.4/5.6 | [21] |
| TCzTRZ  | ITO/PEDOT:PSS/TAPC/mCP/40 wt% TCzTrz:DPEPO/TSPO1/TPBi/LiF/Al | 480 | (0.18, 0.33) | – | 25/42.7/– | $\approx$24.0/15.0 | [22] |
| 234CzTRZ| ITO/PEDOT:PSS/TAPC/mCP/DPEPO:30% 234CzTrz/TPBi/LiF/Al | 497 | (0.20, 0.44) | – | 3.6 | 20.4/14.5 | [23] |
| 235CzTRZ| ITO/PEDOT:PSS/TAPC/mCP/DPEPO:30% 235CzTrz/TSPO1/TPBi/LiF/Al | 495 | (0.20, 0.45) | – | 3.6 | 18.7/14.5 | [23] |
| 245CzTRZ| ITO/PEDOT:PSS/TAPC/mCP/DPEPO:30% 245CzTrz/TSPO1/TPBi/LiF/Al | 490 | (0.17, 0.19) | – | 3.6 | 22/18.0 | [23] |
| 5Cz–TRZ | ITO/HAT–CN/(α–NPD)/Tris–PCz/mCBP | 486 | – | – | 29.3/– | $\approx$29.0/28.6 | [24] |

Figure 10. Comparison of TADF emitters with and without a phenylene bridge between triazine and carbazole derivatives.
In lieu of an indolocarbazole donor, compound CC2TA\(^{[26]}\) (\(\lambda_{\text{PL}}\): 490 nm; \(\tau_{\text{d}}\): 22 µs; \(\Delta E_{\text{ST}}\): 0.06 eV; \(\Phi_{\text{PL}}\): 62%; 6 wt% in DPEPO) contains a carbazole dendrypeptide donor structure. CC2TA exhibited a much improved \(\Phi_{\text{PL}}\) of 62% (6 wt% in DPEPO) as well as a reduced \(\Delta E_{\text{ST}}\) (0.06 eV) compared to PIC–TRZ, and the corresponding device showed an EQEmax of 11%. DTDC (\(\Delta E_{\text{ST}}\): 0.14; \(\tau_{\text{d}}\): 170 µs; \(\Phi_{\text{PL}}\): 61.3%; 6 wt% in DPEPO) and BDTC (\(\Delta E_{\text{ST}}\): 0.09; \(\tau_{\text{d}}\): 260 µs; \(\Phi_{\text{PL}}\): 60.5%; 6 wt% in DPEPO), each containing only one functionalized carbazole donor, were also prepared by Adachi and co-workers.\(^{[27]}\) These two compounds are randomly oriented in the neat films; however, the orientation of the TDMs (orientation order parameter \(\theta\) --0.18 for DTDC; --0.12 for BDTC) of these two TADF emitters is significantly more horizontally aligned when they are dispersed in the DPEPO matrix. The best OLEDs showed comparable efficiencies to that of the CC2TA device with EQEmax values of 10.3% and 11.6% for the DTDC and BDTC devices, respectively. Adachi et al.\(^{[28]}\) also performed a study to elucidate the importance of the bridging phenylene by comparing CzT (\(\lambda_{\text{PL}}\): 502 nm; \(\Delta E_{\text{ST}}\): 0.09 eV; \(\tau_{\text{d}}\): 53 µs; \(\Phi_{\text{PL}}\): 96%; 6 wt% in DPEPO) with BCzT (\(\lambda_{\text{PL}}\): 483 nm; \(\Delta E_{\text{ST}}\): 0.3 eV; \(\tau_{\text{d}}\): 33 µs; \(\Phi_{\text{PL}}\): 96%; 6 wt% in DPEPO) and demonstrated that the bridging phenylene contributes to increasing the overlap density between the electronic wave functions of the ground state and the lowest excited singlet state, leading to both a larger \(\Delta E_{\text{ST}}\) and higher \(\Phi_{\text{PL}}\), yet surprisingly a blue-shifted \(\lambda_{\text{PL}}\). CzT, first reported in 2013 by Adachi et al.,\(^{[28]}\) shows a small \(\Delta E_{\text{ST}}\) of 0.09 eV. The reported OLED shows an EQEmax of only 6% due to the relatively low \(\Phi_{\text{PL}}\) of 40%. The \(\Delta E_{\text{ST}}\) is significantly enhanced, leading to a much higher \(\Phi_{\text{PL}}\) of 96% (6 wt% in DPEPO), while the emission blue-shifted by 19 nm with a higher doping concentration in DPEPO matrix. Despite BCzT obtaining a near unity \(\Phi_{\text{PL}}\), the observed \(\Delta E_{\text{ST}}\) was dramatically raised to 0.3 eV. Despite the larger \(\Delta E_{\text{ST}}\), the delayed fluorescence lifetimes are of a similar magnitude, which can only be explained by the implication of intermediate triplet states in the RISC process of BCzT. The BCzT-based sky-blue OLED exhibits an EQEmax of 21.7% with \(\lambda_{\text{PL}}\) at 492 nm, which is significantly improved compared to the 6% EQEmax of the CzT-based OLED. The photophysical and electrochemical data of the aforementioned materials are summarized in Table 3. Representative device performance is summarized in Table 4.

### Table 3. Summary of photophysical and electrochemical properties.

| Emitter    | Solution \(\lambda_{\text{hu}}/\Phi_{\text{hu}}/\tau_{\text{hu}}\) (medium) [nm/%/μs] | Solid State \(\lambda_{\text{hu}}/\Phi_{\text{hu}}/\tau_{\text{hu}}\) (medium) [nm/%/μs] | \(\Delta E_{\text{ST}}\) [eV] | HOMO [eV] | LUMO [eV] | Ref. |
|------------|----------------------------------|-----------------------------------------------------------------|-----------------|--------|--------|-----|
| PIC–TRZ    | /35/120 (PhMe)                   | /39/120 (6 wt% in mCP)                                          | 0.11            | –      | –      | [25]|
| CC2TA      | 435/–/– (cyclohexane)            | ≈490/62/22 (6 wt% in DPEPO)                                     | 0.06            | –      | –      | [26]|
| CzT        | 512/45.6/42.6 (PhMe)             | 502/39.7/– (3 wt% in DPEPO)                                     | 0.09            | –      | –      | [28]|
| DTDC       | /–/–/–                           | 494/61.3/0.17 ms (6 wt% in DPEPO)                               | 0.14            | 5.80   | 2.60   | [27]|
| BDTC       | /–/–/–                           | 504/60.5/0.26 ms (6 wt% in DPEPO)                               | 0.09            | 5.70   | 2.70   | [27]|
| BCzT       | 460/–/– (PhMe)                   | 483/95.6/33 (6 wt% in DPEPO)                                    | ≈0.30           | –      | –      | [28]|

### Table 4. Summary of device structures and performances.

| Emitter    | Device Structure               | \(E_{\text{Lmax}}\) [nm] | CIE  | \(V_{\text{on}}\) [V] | EQE/PE/CE\(^{0}\) [%/lm W\(^{-1}\)/cd A\(^{-1}\)] | EQE\(_{00}/1000\) [cd] [m\(^{-2}\)] | Ref. |
|------------|--------------------------------|-----------------|------|-----------------|---------------------------------|---------------------------------|-----|
| PIC–TRZ    | ITO/α–NPD/m–CP/6 wt%–PIC–TRZ.m–CP/BP4mPy/LiF/Al | ≈500            | –    | –               | 0.053/–/–                      | NA                             | [25]|
| CC2TA      | ITO/α–NPD/6 wt% CC2TA:mCP/6 wt% CC2TA:DPEPO/DPEPO/TPBI/LiF/Al | 490            | –    | –               | 0.11/–/–                       | NA                             | [26]|
| CzT        | ITO/α–NPD/TCTA/CzSi/3 wt% CzT:DPEPO/DPEPO/TPBI/LiF/Al | 520 (0.23, 0.40) | –    | –               | 0.06/9.7–                      | NA                             | [28]|
| DTDC       | glass/ITO/α–NPD/TCTA/mCP/6 wt% DTDC:DPEPO/TPBI/LiF/Al | ≈500            | –    | 3.8             | 10.3/–/–                       | NA                             | [27]|
| BDTC       | glass/ITO/α–NPD/TCTA/mCP/6 wt% BDTC:DPEPO/TPBI/LiF/Al | ≈540            | –    | 4.7             | 11.6/–/–                       | NA                             | [27]|
| BCzT       | ITO/α–NPD/m–CBP/6 wt% BCzT:DPEPO/TPBI/LiF/Al | 492            | –    | –               | 21.7/–/–                       | NA                             | [28]|

4. Orientation of TADF Materials Containing TRZ and Carbazole/Carbazole Derivatives as Donors

The EQE of the OLEDs also depend on the orientation of the TDM of the emitters, which affects the light out-coupling.
efficiency of the device.\cite{30} Wang et al.\cite{31} prepared two TADF emitters IndCzpTr-1 ($\Phi_{PL}: 75.2\%$, 10 wt\% in mCBP) and IndCzpTr-2 ($\Phi_{PL}: 71.9\%$, 20 wt\% in mCBP) containing an indolocarbazole-based donor (Figure 11). IndCzpTr-2 possesses a slightly smaller $\Delta E_{ST}$ of 0.11 eV than the 0.13 eV for IndCzpTr-1. The more extended structure of IndCzpTr-2 leads to a preferential horizontal orientation of the TDM in the neat film with an orientation order parameter, $S$, of $-0.264$ (estimated by VASE). The $S$ value of IndCzpTr-1 in the neat film is only $-0.1$, which is far away from the theoretical value of $S = -0.5$ for a perfectly horizontal orientation of the TDM. From these measurements in neat films, the orientation factor $\theta$ was calculated as 0.70 for IndCzpTr-1 and 0.77 for IndCzpTr-2, where a value of 1 indicates a perfectly horizontally aligned TDM and a value of 0.66 indicates an isotropic orientation. As a result of greater horizontal orientation of the TDM of IndCzpTr-2, there is a strong divergence in the efficiencies of the OLEDs. The optimized OLEDs within this study realized EQE$_{max}$ values of 14.5\% and 30.0\% for IndCzpTr-1 ($\lambda_{EL}: 472$ nm; CIE = (0.17, 0.27)) and IndCzpTr-2 ($\lambda_{EL}: 496$ nm; CIE = (0.23, 0.50)), respectively. Even though the EQE$_{max}$ of the device with IndCzpTr-1 only reached 14.5\%, it is still much improved compared with PIC-TRZ, demonstrating the link between improved performance and the presence of the phenylene bridge, as both compounds contain the same donor and diphenyltriazine acceptor.

![Figure 11. Molecular structures of triazine-based TADF emitters with/without preference of horizontal orientation in films.](image-url)
The emitter DACT-II \((\Delta E_{ST}: 0.009 \text{ eV}; \Phi_{PL}: 100\% \text{ as 9 wt\% doped film in CBP})\)\(^{[32]}\) is a derivative of Cz-TRZ but contains peripheral diphenylamino groups decorating the Cz donor. Their addition significantly strengthens the donor and turns on TADF compared to Cz-TRZ. DACT-II exhibits a near zero \(\Delta E_{ST}\) of 0.009 eV yet a large oscillator strength, \(f\), reflected in the unity \(\Phi_{PL}\) (9 wt\% in CBP film). These desirable traits translate into a green OLED that shows an impressive EQE\(_{\text{max}}\) of 29.6\% with \(\lambda_{\text{EL}} \approx 520\) nm. The high efficiency of the device is also due to the preferential horizontal orientation of the TDM of DACT-II as determined by VASE measurements \((S = -0.32)\) in Figure 12a and angular-dependent PL measurements \((S = -0.29)\) in Figure 12b. Kim et al.\(^{[33]}\) later showed that efficiency roll-off can be suppressed in the OLED if the CBP host is replaced by a TCTA:B3PYMPM exciplex-forming host, as the authors found a 1.5-fold increased RISC rate in this system \((k_{\text{RISC}}: \text{CBP } 1.37 \times 10^8 \text{ s}^{-1}; \text{TCTA:B3PYMPM } 2.06 \times 10^8 \text{ s}^{-1})\). As a result, the device gives a higher efficiency with an EQE\(_{\text{max}}\) of 34.2\%, which only slightly decreased to 31\% at a luminescence of 1000 cd m\(^{-2}\).

However, the close structural analog, 3CzTRZ\(^{[34]}\) \((\lambda_{\text{PL}}: 468\text{ nm}; \tau_{\text{d}}: 415\mu\text{s}; \Delta E_{ST}: \text{not reported}; \Phi_{PL} 72\%; 6 \text{ wt\% in PPT})\), seems to be oriented randomly in the solid state. 3CzTRZ presents a blue-shifted emission at 468 nm and a lower \(\Phi_{PL}\) of 72\% as a 6 wt\% doped PPT film compared with DACT-II (9 wt\% in CBP). The OLED with 3CzTRZ thus shows much poorer performance with an EQE\(_{\text{max}}\) of 10.5\% \((\lambda_{\text{EL}}: 480\text{ nm}; \text{CIE } = (0.17, 0.26))\), which implies that there is not even a 100\% IQE, assuming an outcoupling efficiency of 0.2–0.25 based on an isotropic orientation of the TDM. However, a structural analog of 3CzTRZ, TCzTRZ \((\Delta E_{ST}: 0.01 \text{ eV}; \Phi_{PL}: 99\%; 10 \text{ wt\% in DPEPO})\), developed by Lee et al.\(^{[14]}\) who replaced the C–N bonded tercarbazole dendron of 3CzTRZ with a C–C bonded tercarbazole dendron, does show 95\% horizontal orientation of the TDM; a similar analog, BCzTRZ, also shows a horizontal dipole orientation of its TDM as high as 89\%, indicating the preferential in-plane alignment is formed both in tercarbazole and bicarbazole-containing compounds. Thus, subtle changes in molecular design can have profound effects on both the propensity for horizontal orientation of the TDM and the efficiency of the device. The \(\Phi_{PL}\) values of the 10 wt\% doped DPEPO film are 99\% and 96\% for TCzTRZ and BCzTRZ, respectively, both of which are significantly higher than that of 3CzTRZ (72\% in DPEPO matrix). Thanks to the near unity \(\Phi_{PL}\) and near perfect horizontal

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**Figure 12.** a) Results of VASE measurements; extinction coefficient \(k\) (black) and refractive index \(n\) (red). The solid and dashed lines represent spectra for the ordinary and extraordinary optical constants, respectively. b) Results of angular-dependent PL experiments. c) Optical simulations for the DACT-II-9 device. The numbers in parentheses for respective modes are obtained by the integration with respect to emission wavelengths with weighting of the PL intensity. d) Dependence of the out-coupling mode on the thicknesses of hole and electron-transport layers.\(^{[32]}\)
orientation, the blue OLED shows an outstanding EQEmax of 31.8% at a $\lambda_{EL}$ of 496 nm and CIE coordinates of (0.20, 0.44).

TRZ-DI ($\Delta E_{ST}$: 0.023 eV), designed by Kwon et al.,\textsuperscript{[35]} incorporates a $D_3$-symmetric triazatruxene donor. Compared with Cz in Cz-TRZ, the extended conjugation within triazatruxene effectively localizes the HOMO only on the donor group, leading to a very small $\Delta E_{ST}$ of 0.02 eV. A small dihedral angle (24.5°) between the plane of triazatruxene and the TRZ acceptor, along with the rigid molecular structure, contributes to a very small $\Phi_{PL}$ of 87% (25 wt% in TCTA: Bepp2 exciplex host). A green OLED using TRZ-DI [$\lambda_{EL}$: 526 nm; CIE = (0.31, 0.57)] as the emitter exhibits an outstanding EQEmax of 31.4%. The orientation of the TDM of TRZ-DI was not investigated, but it is not unreasonable to hypothesize that TRZ-DI possesses a highly horizontally oriented TDM based on the analysis of the $\Phi_{PL}$ and the EQEmax.

TRZ–SBA–NAI ($\Delta E_{ST}$: 0.16 eV; $\Phi_{PL}$: 87%; 3 wt% in mCPCN), designed by Yang et al.,\textsuperscript{[36]} contains an A–D–A’ motif, where a spirobiacridine (SBA) donor is used to link the acceptors NAI and TRZ, as shown in Figure 13. Because of the weak electronic communication through the central sp3 carbon on the SBA donor, two distinct CT emission bands at $\lambda_{PL}$ of around 474 and 586 nm were observed in toluene, with the former assigned to TRZ–SBA and the later to SBA–NAI. By contrast, the solid-state emission 3.0 wt% doped in mCPCN matrix only showed a band at $\lambda_{PL}$ of 577 nm from the SBA–NAI moiety, suggesting efficient energy conversion from the high-lying excited states of TRZ–SBA to SBA–NAI. The different PL character in toluene and film was ascribed to the higher intramolecular charge transfer rate via FRET to the radiative decay rate of the TRZ–SBA counterpart. The TDM vector aligns with the molecular long axis, which contributes to the high horizontal dipole ratios ($\Theta_{||}$) of 88% in the mCPCN host matrix (Figure 14). Finally, the orange-red OLED based on TRZ–SBA–NAI showed an EQEmax of 31.7% at $\lambda_{EL}$ of 593 nm and CIE coordinates of (0.55, 0.45).

A similar design using SBA as the donor and triazine as the acceptor has also been explored by Kido et al.\textsuperscript{[37]} to enable the horizontal orientation of the TDM of emitters in OLEDs. Three molecules, tBuTZ-SBA-Ph, TZ-SBA-Ph, and tBuPhTZ-SBA-Ph, were prepared with the difference in structure associated with the choice of distal groups on the triazine acceptor unit. The $\Phi_{PL}$ values of tBuTZ-SBA-Ph, TZ-SBA-Ph, and tBuPhTZ-SBA-Ph in toluene are modest at 34%, 55%, and 43%, respectively. However, the $\Phi_{PL}$ values in neat films increased to 41% for tBuTZ-SBA-Ph, 90% for TZ-SBA-Ph, and 65% for tBuPhTZ-SBA-Ph. By comparing with the $\Phi_{PL}$ values of the 10 wt% doped films in DPEPO matrix (87% for tBuTZ-SBA-Ph, 100% for TZ-SBA-Ph, and 97% for tBuPhTZ-SBA-Ph), the similarly high $\Phi_{PL}$ values for TZ-SBA-Ph in both neat and doped films indicate a strong suppression of intermolecular concentration quenching. The orientation ratio ($\Theta_{||}$) in evaporated doped films was quantified to be 56%, 82%, and 82% for tBuTZ-SBA-Ph, TZ-SBA-Ph, and tBuPhTZ-SBA-Ph, respectively, as shown in Figure 15. The larger $\pi$-plane in TZ-SBA-Ph and tBuPhTZ-SBA-Ph, as asserted by the authors, would be more likely to interact with the deposition surface, thus enhancing the horizontal orientation. The OLEDs achieved EQEmax of 24.1%, 31.2%, and 28.3% for the devices with tBuTZ-SBA-Ph, TZ-SBA-Ph, and tBuPhTZ-SBA-Ph, respectively. The
performance is in line with the properties in doped films in terms of $\Phi_{PL}$ and $\Theta$ values. The photophysics and electrochemical characteristics of the aforementioned materials are summarized in Table 5, and representative device performance metrics are summarized in Table 6.

5. Symmetric Substitution of Carbazole/Carbazole Dendrons on Triphenyltriazine Core

In this section, we focus on trisubstituted triazine-based dendrimer emitters. The very first TADF dendrimers, GnTAZ

Figure 14. a) Isodensity surface of TRZ–SBA–NAI with $\rho = 0.001$ e bohr$^{-1}$ and their spatial range in the Cartesian axes based on optimized $S_0$ structure. b) The direction of the calculated $S_0$–$S_1$ transition dipole moment (as indicated by the arrow) of TRZ–SBA–NAI based on the optimized $S_1$ structure. c) Measured $p$-polarized PL intensity (at PL peak wavelength) versus emission angle curve of 3.0 wt% TRZ–SBA–NAI doped into mCPCN host. Reproduced with permission.[36] Copyright 2021, Royal Society of Chemistry.

Figure 15. PL intensity of 10 wt% a) tBuTZ-SBA-Ph, b) tBuPhTZ-SBA-Ph, and c) TZ-SBA-Ph-doped host films at different angles. The experimental data are compared with the fitting curve for different horizontal dipole ratios (Θ) for X-SBA-Ph derivatives doped in a host film of DPEPO. d) The direction of the calculated $S_0$–$S_1$ transition dipole moment. Reproduced with permission.[37] Copyright 2021, Wiley-VCH.
Table 5. Summary of photophysical and electrochemical properties.

| Emitter        | Solution λ_{PE}/Φ_{PE}/τ_{PE} (medium)       | Solid State λ_{PE}/Φ_{PE}/τ_{PE} (medium)       | ΔE_{ST} | HOMO  | LUMO  | Ref.  |
|----------------|---------------------------------------------|---------------------------------------------|--------|-------|-------|-------|
|                | [nm]/[%]/[μs]                                | [nm]/[%]/[μs]                                |        | [eV]  | [eV]  |       |
| IndCzTrz       | 480/25.48 (2Me-THF)                          | 492/75.2/2.8 (mCBP)                         | 0.13   | -5.47 | -2.91 | [31]  |
| IndCzTrz-2     | 490/34.31 (2Me-THF)                          | 510/71.9/2.9 (mCBP)                         | 0.12   | -5.29 | -2.95 | [31]  |
| 3CzTRZ         | -/-/-                                       | -/6/12/11 (9 wt% in THF)                     | 0.06   | 5.31  | 2.97  | [14]  |
| DACT-I         | -/-/-                                       | -/96/11.2 (10 wt% in DPEPO)                 | 0.04   | -5.8  | -3.24 | [14]  |
| DACT-I         | -/63.7/- (PhMe)                             | ≈520/100/- (9 wt% in CBP)                   | 0.009  | 5.5   | 3.2   | [32]  |
| BcCzTrz        | -/-/-                                       | -/96/11.2 (10 wt% in DPEPO)                 | 0.04   | -5.8  | -3.24 | [14]  |
| TcCzTrz        | -/-/-                                       | -/99/23.6 (10 wt% in DPEPO)                 | 0.01   | -5.75 | -3.41 | [14]  |
| TRZ-DI         | 506/-/1.61 (PhMe)                           | 521/87/1.32 (25 wt% TCTA:Bepp2)             | 0.023  | 5.7   | 3     | [35]  |

Table 6. Summary of device structures and performance.

| Emitter        | Device Structure                  | EL_{max}  | CIE      | V_{on} | EQE/PE/CE | EQE_{100/1000} |
|----------------|----------------------------------|-----------|----------|--------|-----------|----------------|
|                | [V]                              | [lm/W]    | [%]      | [lm/W] | [cd/A]    | [cd/m²]        |
| IndCzTrz-1     | ITO/MoO3/TACP/mCP/EML/DPEPO/TmPyPB/LiF/Al | 472       | 0.17     | 0.27   | 3.8       | 14.5/23.2/28.1/11.0/6.7/3.5 | [31] |
| IndCzTrz-2     | ITO/MoO3/TACP/mCP/EML/DPEPO/TmPyPB/LiF/Al | 496       | 0.23     | 0.50   | 4        | 30/61.8/82.6/15.3/11  | [31] |
| 3CzTRZ         | ITO/HAT- CN-Tris-PCz-10 wt% 3CzTrz-PPT/LPT/LiF/Al | 480       | 0.17     | 0.26   | 4        | 34.2/121.3/114/26.5/10 | [32] |
| DACT-I         | ITO/TACP TRZ-10 wt% DACT-II/96/11.2/C25 | ≈520      | -        | -      | -9       | 29.6/14/36 | [32] |
| BcCzTrz        | ITO/PEDOT:PPS/TACP/cmp/10 wt% BcCzTrz in DPEPO/TSP1/TBP/LiF/Al | 485       | 0.23     | 0.42   | -        | 23.6/46.6/53.3/15/6 | [14] |
| TcCzTrz        | ITO/PEDOT:PPS/TACP/cmp/10 wt% TcCzTrz in DPEPO/TSP1/TBP/LiF/Al | 496       | 0.20     | 0.44   | -        | 31.8/61.5/86.4/26/16 | [14] |
| TRZ-DI         | ITO/HATCN/NPB/TACP/C25/Bepp2:25%/TRZ-DI/TmPyPB/LiF/Al | 526       | 0.31     | 0.57   | 2.6      | 31.4/91.6/87.5/30/29 | [35] |

(n refers to the generation of the dendron) (Figure 16), were developed by Yamamoto et al.[38] These compounds contain three symmetrical carbazole donor dendrons (from second generation to fourth generation; 1st generation with only Cz as the donor was not studied due to the insolubility of this compound) attached to a central TRZ acceptor. All three dendrimers showed near unity Φ_{PE} and very small ΔE_{ST} in toluene solution: G2TAZ (ΔE_{ST} = 0.03 eV; Φ_{PE} = 94% in toluene), G3TAZ (ΔE_{ST} = 0.06 eV; Φ_{PE} = 100% in toluene), and G4TAZ (ΔE_{ST} = 0.06 eV; Φ_{PE} = 94% in toluene). However, the Φ_{PE} decreased significantly for the neat films to 52%, 31%, and 8.5%, respectively, which was rationalized in terms of increasing concentration quenching in the neat films along the series. OLEDs with neat films of GnTAZ dendrimers as the emitting layer performed poorly, with the highest EQEmax of 3.4% at CIE coordinates of (0.27, 0.49) for the device with G3TAZ.

Yamamoto et al.[39] showed how substitution about the periphery of the donor dendron in G2TAZ analogs can affect the Φ_{PL}. Compared to G2TAZ, methyl (MeG2TAZ) (Φ_{PL} = 40%; τ_{PL} = 3.3 μs; ΔE_{ST} = 0.07 eV; in neat film), tert-butyl (BuG2TAZ) (Φ_{PL} = 45%; τ_{PL} = 5.3 μs; ΔE_{ST} = 0.07 eV; in neat film), phenyl (PhG2TAZ) (Φ_{PL} = 49%; τ_{PL} = 1.9 μs; ΔE_{ST} = 0.08 eV; in neat film), and 7H-dibenzo[cd]carbazole (dbG2TAZ) (Φ_{PL} = 9.1%; ΔE_{ST} = 0.53 eV; in neat film) analogs all showed similar PL spectra and comparably high Φ_{PL} in toluene, with BuG2TAZ showing the highest Φ_{PL} of 96%. These dendrimers suffered a similarly lower Φ_{PL} as neat films compared to toluene solutions. Apart from dbG2TAZ, which has the lowest Φ_{PL} in the neat film, all of the other dendrimers have only modestly lower Φ_{PL} than G2TAZ (52%). However, the EQEmax based on the solution-processed OLEDs improved from 6.0% (G2TAZ) to 9.4% (MeG2TAZ), 9.5% (tBuG2TAZ), and 8.2% (PhG2TAZ), respectively.

Although the EQEmax of the OLED based on tBuG2TAZ improved to 9.5%, this performance is still not comparable to the efficiencies reported for nondoped vacuum-deposited devices based on small-molecule TADF emitters. This is due to the low Φ_{PL} (∼50%) in the neat film that results from concentration quenching. To solve the problem and further improve the device performance, Yamamoto et al.[40] developed two carbazole-based dendrimers (G3Ph and G4Ph as shown in Figure 17) as host materials to suppress the observed concentration quenching of tBuG2TAZ (Φ_{PL} = 50 nm; Φ_{PL} = 76%; ΔE_{ST} = 0.07 eV; 15 wt% in G3Ph). The doping concentration of 15% was chosen to optimize the Φ_{PL} in the blended film. The emission spectra remain unchanged at 500 nm between the neat film and the films doped in G3Ph and G4Ph. However, the Φ_{PL} increased from 44% in neat film to 76% and 70% in G3Ph and G4Ph (15 wt%), respectively. The EQEmax of the green-emitting OLED was significantly improved to 16.1% at CIE coordinates of (0.28, 0.49).

Recently, our group[41] has developed a series of green TADF dendrimers that contain carbazole dendron donors surrounding a TRZ core acceptor unit, linked via either a para-/meta-phenoxy (BuCz2m2pTRZ / BuCz2m2pTRZ) or combination of both connections (BuCz2m2m2pTRZ), as shown in Figure 18. The design strategy of BuCz2m2pTRZ (Φ_{PL} = 520 nm; Φ_{PL} = 86%; ΔE_{ST} = 0.04 eV; neat film) demonstrates that BuCz2m2pTRZ...
Figure 16. Molecular structures and properties of TADF dendrimer emitters with symmetric trisubstitution of carbazole dendrons.

|     | G2TAZ                                | G3TAZ                                | G4TAZ                                |
|-----|--------------------------------------|--------------------------------------|--------------------------------------|
| λ<sub>ex</sub> (nm) | 473                                 | 473                                 | 473                                 |
| τ<sub>CP</sub> (μs)  | N/A                                 | N/A                                 | N/A                                 |
| ΔE<sub>CT</sub> (eV) | 0.07, 0.03 eV                        | 0.06 eV                             | 0.06 eV                             |
| Φ<sub>PL</sub> (%) | 94%                                 | 100%                                | 100%                                |
| λ<sub>EL</sub> (nm) | ~510                                 | ~510                                 | ~510                                 |
| EQE<sub>max</sub> (%) | 2.4%                                | 3.4%                                | 1.5%                                |

Figure 17. Molecular structures of dendrimer host materials G3Ph and G4Ph.
is capable of inheriting key properties from both tBuCz2pTRZ ($\lambda_{PL}: 481$ nm; $\Phi_{PL}: 61\%$; $\Delta E_{ST}: 0.09$ eV; neat film) and tBuCz2mTRZ ($\lambda_{PL}: 483$ nm; $\Phi_{PL}: 59\%$; $\Delta E_{ST}: 0.09$ eV; neat film), with the excited-state behavior being modulated as a result of the interactions between the two adjacent donor dendrons. The para-connection of the donor dendrons in tBuCz2m2pTRZ leads to strong electronic coupling between donor and acceptor, as evidenced by the strong molar absorption for the ICT transition, while the additional meta-connection in tBuCz2m2pTRZ results in a small $\Delta E_{ST}$ as the meta-disposed donor and acceptor groups are electronically decoupled. The $\lambda_{PL}$ of tBuCz2pTRZ is similar to that of tBuCz2mTRZ, indicating similar energies of their 1CT states regardless of the electronic coupling between donor and acceptor. The spectral red-shift of tBuCz2m2pTRZ indicates the stabilized 1CT states with more dendritic moieties than tBuCz2pTRZ and tBuCz2mTRZ. Nondoped solution-processed OLEDs using a simple device configuration (Figure 19) without exciton barrier layers and containing only the dendrimers in the emissive layer exhibited the EQE max of 18.5%, 19.9%, and 28.7% for tBuCz2pTRZ, tBuCz2mTRZ, and tBuCz2m2pTRZ.

Figure 18. Molecular structures and properties of TADF dendrimer emitters with symmetric disubstitution of carbazole dendrons. Reproduced with permission.[41] Copyright 2022, Wiley-VCH.

Figure 19. Electroluminescence characteristics of host-free OLEDs using tBuCz2pTRZ, tBuCz2mTRZ, and tBuCz2m2pTRZ as emitters. a) Device configuration. b) Normalized electroluminescence spectra. c) Current density and luminance versus driving voltage characteristics. d) EQE versus brightness for tBuCz2pTRZ (black), tBuCz2mTRZ (red), and tBuCz2m2pTRZ (blue) based devices. (The photos shown from bottom left to right for tBuCz2pTRZ, tBuCz2mTRZ, and tBuCz2m2pTRZ-based devices, respectively). e) Statistical histogram of EQE_max for tBuCz2m2pTRZ-based OLEDs. f) The EQE_max of all reported solution-processed host-free TADF OLEDs as a function of wavelength.
respectively. The performance of the device with tBuCz3m2pTRZ represents a step change in the efficiency of the nondoped solution-processed OLEDs. Importantly, the efficiency roll-off of the OLED based on tBuCz2m2pTRZ is significantly improved by doping 30 wt% OXD-7, an electron-transporting material, into the emissive layer. As a result of the improved charge balance, the EQE of the optimized device not only reached a similar EQEmax of 28.4% but also maintained its efficiency of 22.7% at a luminance of 500 cd m⁻².

A related work documents a detailed photophysical investigation to rationalize the structure–property relationship of the TADF dendrimers tBuCz3pTRZ and tBuCz3mTRZ (the DFT optimized structures without peripheral tert-butyl groups are shown in Figure 19). Both dendrimers exhibit high Φ_pl values (89% for tBuCz3pTRZ and 81% for tBuCz3mTRZ, 10 wt% doped in mCP). While tBuCz3mTRZ (2.92 eV) possesses a slightly higher S1 state than that of tBuCz3pTRZ (2.84 eV) due to the weak electron coupling of meta-connection, both have a similarly small ΔE_ST (0.1 eV for tBuCz3pTRZ and 0.08 eV for tBuCz3mTRZ). The activation energy barriers (E_act) for RISC are approximately half those of the corresponding ΔE_ST values. However, the contribution of the delayed emission to the total emission (19% for tBuCz3pTRZ and 63% for tBuCz3mTRZ) and the k_RISC (0.5 × 10⁸ s⁻¹ for tBuCz3pTRZ and 3.7 × 10⁸ s⁻¹ for tBuCz3mTRZ), both reflecting the efficiency of the RISC process, are much greater/faster in the case of the meta-connected dendrimer tBuCz3mTRZ.

The comparison of the DFT calculation for the model dendrimers without tert-butyl groups is shown in Figure 20. Unlike Cz3pTRZ, Cz3mTRZ has negligible overlap between the hole and electron NTO distribution in the T1 states. This leads to a greater CT character in the T1 state of Cz3mTRZ (ω_Chr= 0.54) as compared to Cz3pTRZ (ω_Chr= 0.38). The calculated spin–orbital coupling (SOC) matrix element was found to be higher for Cz3mTRZ (0.53 cm⁻¹) as compared to Cz3pTRZ (0.31 cm⁻¹). The intramolecular (Δω) reorganization energy for Cz3pTRZ (275 meV) was also calculated to be higher than that of Cz3mTRZ (155 meV). Most TADF molecule design strategies focus on the minimization of the ΔE_ST; however, it is observed that the enhancement of the SOC for the T1 → S1 transition and the reduced reorganization energy also significantly contribute to the faster k_RISC in tBuCz3mTRZ compared to tBuCz3pTRZ, despite their similar ΔE_ST values. This work demonstrates the importance of the regiochemistry of the donor dendrons on the control of the SOC and reorganization energies, which is a heretofore unexploited strategy that is distinct from the involvement of intermediate triplet states through a nonadiabatic (vibronic) coupling with the lowest singlet charge transfer state.

The introduction of tert-butyl groups to carbazole donor dendrons in G1TAZ was reported by Ulanski et al.[43] Dendrimers TR1 and TR2 (Figure 21) contain one and two tert-butyl groups on each carbazole unit, respectively, their inclusion was designed to improve the solubility of the dendrimers. Similar to Cz-TRZ, both TR1 (β_pl: 398 nm; Φ_pl: 83% in hexane) and TR2 (ρ_pl: 407 nm; Φ_pl: 74% in hexane) are deep blue emitters, with only very short lifetimes of a few nanoseconds, suggesting that these dendrimers do not show TADF. A subsequent study compared the para-substituted compound TR2 (renamed as TpCz) with a newly designed meta-linked donor dendron dendrimer TmCz. The photophysical properties of TmCz (β_pl: ~450 nm; Φ_pl: 25%; τ_pl: 80 μs (1 wt% in PMMA); ΔE_ST: 0.125 eV) and TpCz (β_pl: ~440 nm; Φ_pl: 35%; τ_pl: 500 μs (1 wt% in PMMA); ΔE_ST: 0.249 eV) revealed that TpCz possesses a larger oscillator strength leading to a higher Φ_pl, but at the expense of a lower triplet energy, stronger charge transfer character, and larger ΔE_ST. A blue vacuum-deposited OLED using TmCz as the emitter showed an EQEmax of 9.5% at CIE coordinates of (0.16, 0.23) and λ421 at 475 nm, demonstrating that TmCz emits via TADF in the device.

Another design strategy, developed by Sun et al.[45] for TADF dendrimers incorporates nonconjugated aliphatic chains linked to distal carbazole moieties that act as host units. Compounds TZ-Cz and TZ-3Cz (Figure 21) are based on a para-connected

![Figure 20. Natural transition orbital (NTO) pairs for the S1 and T1 states of Cz3pTRZ and Cz3mTRZ. The spin–orbit coupling (SOC) matrix elements are also provided.](image-url)
The authors contend that the emissive core is encapsulated by the nonconjugated dendrons, thus suppressing concentration quenching. Similar to TR1 and TR2, Tz (λ_{PL}: 502 nm; Φ_{PL}: 25%; ΔE_{ST}: 0.28 eV; in neat film) is only a fluorescent emitter and does not show TADF. However, TADF turns on in TZ-Cz (λ_{PL}: 490 nm; Φ_{PL}: 58% in neat film; ΔE_{ST}: 0.20 eV) and TZ-3Cz (λ_{PL}: 487 nm; Φ_{PL}: 76% in neat film; ΔE_{ST}: 0.20 eV), which the authors assert is due to the change in local environment that results from the encapsulation. The best solution-processed OLED was achieved using TZ-3Cz (λ_{EL}: 520 nm; CIE = (0.24, 0.51)) in a host-free configuration and showed a much-improved EQE_{max} of 10.1% compared to the OLED based on Tz (1.09%). The photo- and electrochemical characteristics of the aforementioned materials are summarized in Table 7, and representative device performance metrics are summarized in Table 8.

6. TADF Emitters Containing Two TRZ and Carbazole/Carbazole Derivative Donors

There are a small number of examples of emitters containing two triazine acceptors. Many of these examples are based on a dimerization strategy. As shown in Figure 22, Lee et al.\textsuperscript{46} reported two related green TADF emitters mCBPTRZ-1 (λ_{PL}: 472 nm; Φ_{PL}: 95%; τ_d: 5.65 µs; ΔE_{ST}: 0.20 eV; 10 wt% in DPEPO) and mCBPTRZ-2 (λ_{PL}: 482 nm; Φ_{PL}: 74%; τ_d: 3.21 µs; ΔE_{ST}: 0.19 eV; 10 wt% in DPEPO), which are dimers of the TADF
Table 7. Summary of photophysical and electrochemical properties.

| Emitter | Solution λ_{PL}/Φ_{PL}/τ_{PL} (medium) [nm/%/μs] | Solid State λ_{PL}/Φ_{PL}/τ_{PL} (medium) [nm/%/μs] | ΔE_{ST} [eV] | HOMO [eV] | LUMO [eV] | Ref. |
|---------|---------------------------------|---------------------------------|-------------|---------|---------|------|
| G2TAZ  | 473/94/-(PhMe)                  | –/52/– (in neat film)           | 0.03        | –5.76  | –3.01  | [38] |
| G3TAZ  | 473/100/-(PhMe)                 | –/31/– (in neat film)           | 0.06        | –5.72  | –2.97  | [38] |
| G4TAZ  | 473/94/-(PhMe)                  | –/8.5/– (in neat film)          | 0.06        | –5.68  | –2.80  | [38] |
| MeG2TAZ| –/92/– (PhMe)                   | –/40.3/3.3 (in neat film)       | 0.07        | –5.73  | –2.85  | [39] |
| tBuG2TAZ| –/96/– (PhMe)                 | –/45.3/5.3 (in neat film)       | 0.07        | –5.79  | –2.88  | [39] |
| PhG2TAZ| –/95/– (PhMe)                   | –/49/1.9 (in neat film)         | 0.08        | –5.79  | –2.90  | [39] |
| dbG2TAZ| –/86/– (PhMe)                   | –/9.1/– (in neat film)          | 0.53        | –5.76  | –2.99  | [39] |
| TR1    | 398/83/– (hexane)               | 462/23/– (neat film)            | –           | 5.49   | 2.86   | [43] |
| TR2    | 407/74/– (hexane)               | 466/29/– (neat film)            | –           | 5.70   | 2.83   | [43] |
| TrmCZ  | ≈475/– (PhMe)                   | ≈450/25/80 (in PMMA)            | 0.13        | –5.65  | –2.78  | [44] |
| Tz     | 535/– (DCM)                     | 502/32/– (neat)                 | 0.28        | –5.11  | –2.22  | [45] |
| TZ–Cz  | 535/– (DCM)                     | 490/58/– (neat film)            | 0.20        | –5.20  | –2.31  | [45] |
| TZ–3Cz | 535/– (DCM)                     | 487/76/– (neat film)            | 0.20        | –5.00  | 2.11   | [45] |

Table 8. Summary of device structures and performance.

| Emitter | Device Structure | EL_{max} [V] | CIE | V_{opt} [V] | EQE/Φ/CE [%/%/cd A^{-1}] | EQE_{1000/1000} [cd m^{-2}] | Ref. |
|---------|-----------------|--------------|-----|-------------|--------------------------|-----------------------------|------|
| G2TAZ   | ITO/PEDOT:TBP/TBP/TB/PV/Al | – (0.252, 0.493) | 3.3 | 2.4/–/– | N/A | [38] |
| G3TAZ   | ITO/PEDOT:TBP/TBP/TB/PV/Al | – (0.266, 0.485) | 3.5 | 3.4/–/– | N/A | [38] |
| G4TAZ   | ITO/PEDOT:TBP/TBP/TB/PV/Al | – (0.232, 0.368) | 3.5 | 1.5/–/– | N/A | [38] |
| G2TAZ   | ITO/PEDOT–PVK:G2TAZ/TBP/Al | – – | 3.7 | 6.2/–/– | N/A | [39] |
| MeG2TAZ | ITO/PEDOT–PVK:MeG2TAZ/TBP/Al | – – | 3.0 | 9.4/–/– | 9.4/NA | [39] |
| tBuG2TAZ| ITO/PEDOT–PVK:tBuG2TAZ/TBP/Al | – – | 3.5 | 9.5/–/– | 9.4/NA | [39] |
| PhG2TAZ | ITO/PEDOT–PVK:PhG2TAZ/TBP/Al | – – | 3.2 | 8.2/–/– | 8.0/NA | [39] |
| tBuG2TAZ| A:ITO/PEDOTPS/15 wt% tBuG2TAZ in | 503 (0.28, 0.48) | 2.9 | 16/19/3.22.7 | 40 |
| tBuG2TAZ| A:ITO/PEDOTPS/15 wt% tBuG2TAZ in | 508 (0.29, 0.51) | 2.9 | 10.5/27.3/28.6 | 40 |
| TR1     | ITO/PEDOT–PVK:PB/Al:TR (3 wt%)/LiF/A | 463 (0.15, 0.13) | 8 | –/–/0.51 | N/A | [43] |
| TR2     | ITO/PEDOT–PVK:PB/Al:TR (3 wt%)/LiF/A | 515 (0.21, 0.33) | 9.5 | –/–/0.46 | N/A | [43] |
| TrmCZ   | ITO/m–MTPA/TBP/Al:MeCZ:6.6 | 475 (0.16, 0.23) | 5.0–6.0 | 9.5/–/– | N/A | [44] |
| TZ      | ITO/PEDOT–PVK:TS–Cz/TBP/Al | 520 (0.32, 0.51) | 4.7 | 1.0/–/3.4 | N/A | [45] |
| TZ–Cz   | ITO/PEDOT–PVK:TS–Cz/TBP/Al | 520 (0.24, 0.51) | 4.0 | 6.5/–/20 | N/A | [45] |
| TZ–3Cz  | ITO/PEDOT–PVK:TS–Cz/TBP/Al | 520 (0.24, 0.51) | 3.6 | 10.1/–/30.5 | N/A | [45] |

emitter o-CzTRZ (λ_{PL}: 455 nm; Φ_{PL}: 16.7%; τ_{PL}: 3.90 μs; ΔE_{ST}: 0.10 eV; 5 wt% in mCP). The Φ_{PL} of these two compounds are significantly enhanced compared to that of the parent emitter o-CzTRZ (16.7%). Dimerization is expected to enhance the overlap between frontier molecular orbitals (FMOs), which leads to an increase of the oscillator strength, thus resulting in the higher Φ_{PL}, but at the expense of a red-shifted emission along with a larger ΔE_{ST}. The OLEDs using mCBPTRZ-1 (λ_{PL}: 503 nm; CIE = (0.23, 0.52)) emits in the green with an EQE_{max} of 20.8%, while the device using mCBPTRZ-2 (λ_{PL}: 521 nm; CIE = (0.31, 0.59)) that contains the more electron-rich 3,6-di-tert-butylcarbazole shows a red-shifted emission and a significantly lower EQE_{max} of 9.3% despite of the high Φ_{PL} of the emitter. The low device efficiency was rationalized by the authors as due to the weak exciton conversion efficiency of 41% in the mCBPTRZ-2-based device compared to 90% in the mCBPTRZ-1-based device. However, this explanation does not seem plausible given their similar molecular structures and photophysics.

Lee et al. also reported two triazine analog emitters to 2CzTPN and 2CzTPN, p2CzTRZ and m2Cz2TRZ (Figure 22), which contain ortho-disposed carbazole units to the bis(diphenyltriazine) moiety. According to the computed FMOs in Figure 23, the HOMO of p2Cz2TRZ and m2Cz2TRZ are evenly distributed over two carbazole donors whereas the LUMOs are evenly
distributed over the two TRZ acceptors. A strong overlap between the HOMO and LUMO at the central phenyl moiety contributes to the high $\Phi_{PL}$. Compounds $\text{p2Cz2TRZ}$ ($\lambda_{PL}$: 505 nm; $\Phi_{PL}$: 86%; $\tau_d$: 16.6 $\mu$s; $\Delta E_{ST}$: 0.18 eV; 10 wt% in DPEPO) and $\text{m2Cz2TRZ}$ ($\lambda_{PL}$: 510 nm; $\Phi_{PL}$: 96%; $\tau_d$: 12.2 $\mu$s; $\Delta E_{ST}$: 0.09 eV; 10 wt% in DPEPO) each showed green delayed fluorescence, with $\text{m2Cz2TRZ}$ having a higher $\Phi_{PL}$ and a smaller $\Delta E_{ST}$ than $\text{p2Cz2TRZ}$. The OLED with $\text{m2Cz2TRZ}$ showed a correspondingly higher EQE$_{max}$ of 18.5% coupled with a bluer emission ($\lambda_{EL}$: 493 nm; CIE $\approx$ (0.20, 0.47)] compared with the device using $\text{p2Cz2TRZ}$, which showed an EQE$_{max}$ of 12.5% [$\lambda_{EL}$: 534 nm; CIE $\approx$ (0.39, 0.58)].

Kwon et al.$^{[35]}$ used a diindolocarbazole as a central donor core to connect two diphenyltriazine TRZ and carbazole/carbazole derivative donors. Figure 22. Molecular structures and properties of TADF emitters based on two diphenyltriazine TRZ and carbazole/carbazole derivative donors.

Figure 23. Calculated HOMO and LUMO distributions of the $\text{p2Cz2TRZ}$ and $\text{m2Cz2TRZ}$. Reproduced with permission.$^{[47]}$ Copyright 2017, Elsevier.
The dimerization strategy (Figure 24) could also be used to convert a non-TADF emitter into a TADF emitter, as Lee et al. [48] demonstrated by transforming the fluorescent emitter Cz-TRZ into a TADF emitters (TRZoCz and TRZoTzCz) by increasing the separation of the FMOs in the dimer structures. The highly twisted geometries in TRZoCz and TRZoTzCz lead to markedly smaller $\Delta E_{ST}$ (0.20 eV for TRZoCz, 0.06 eV for TRZoTzCz) compared to Cz-TRZ (0.36 eV). The $\Phi_{PL}$ of TRZoCz and TRZoTzCz are 96% and 98%, respectively, for the 10 wt% films in DPEPO. The PL spectra are red-shifted compared to that of Cz-TRZ due to the increased conjugation within their structures, the photophysics of the two compounds are also less sensitive to the doping concentration. The EQE max of the two emitters, the photophysics of the two compounds are also less sensitive to the doping concentration.

7. Modification to the Phenylene Bridge

The degree of orbital overlap between the HOMO and LUMO is controlled not only by the choice of donor and acceptor but also by the bridging unit that mediates the conjugation between the two. For example, the introduction of a methyl group or phenyl group onto the phenylene bridge affects one of the torsion angles, leading to a more twisted conformation and thus a smaller $\Delta E_{ST}$, while the inclusion of more strongly electron-withdrawing groups such as nitrile or trifluoromethyl substituents also contributes to strengthening the electron-acceptor and localizing the electron density of the LUMO.

Buchwald et al. [49] reported a series of TADF emitters (Figure 25) that incorporate a triptycene-fused carbazole donor para-linked to a diphenyltriazine acceptor via a arylene bridge. The dihedral angle between donor and the bridging arylene was manipulated by controlling the position and number of methyl substituents. Compared with TCZTRZ (3.97 nm; $\Phi_{PL}$: 40%; $\tau_d$: 38 μs; $\Delta E_{ST}$: 0.27 eV; 15 wt% in DPEPO), the introduction of a methyl group on the arylene bridge at a position adjacent to TRZ in TCZTRZ(Me) (3.94 nm; $\Phi_{PL}$: 51%; $\tau_d$: 58 μs; $\Delta E_{ST}$: 0.12 eV; 15 wt% in DPEPO) results in a higher $\Phi_{PL}$ along with a reduced $\Delta E_{ST}$ due to the increased angle (25.1°) between the arylene plane and the TRZ plane despite the identical angle (51.5°) between the plane of triptycene-fused carbazole and the arylene plane. Placement of the methyl group close to the donor elicits a similar outcome. Emitter TCZTRZ(Me) (3.95 nm; $\Phi_{PL}$: 32%; $\tau_d$: 51 μs; 15 wt% in DPEPO; $\Delta E_{ST}$: 0.16 eV) also possesses a twisted structure with the torsion angle increased from 51.5° in TCZTRZ to 69.5° in TCZTRZ(Me). The $\Delta E_{ST}$ of TCZTRZ(Me) is smaller as well at 0.16 eV; however, at a cost of a lower $\Phi_{PL}$ of 32%. The addition of a second methyl group on the arylene bridge in

![Figure 24](www.advancedsciencenews.com) Design strategy for the TADF molecule TRZoCz. Reproduced with permission [48]. Copyright 2020, Wiley-VCH.

Table 9. Summary of photophysical and electrochemical properties.

| Emitter       | Solution $\lambda_{PL}/\Phi_{PL}/\tau_d$ (medium) | Solid State $\lambda_{PL}/\Phi_{PL} (\mu s)$ | $\Delta E_{ST}$ [eV] | HOMO [eV] | LUMO [eV] | Ref. |
|---------------|-----------------------------------------------|------------------------------------------|---------------------|-----------|-----------|------|
| mCBPTrz−1     | −/−/− (THF)                                   | 472/55/6.5 (10 wt% in DPEPO)              | 0.20                | −6.11     | −3.32     | [46] |
| mCBPTrz−2     | −/−/− (THF)                                   | 482/74/3.21 (10 wt% in DPEPO)             | 0.19                | −6.01     | −3.22     | [46] |
| p2Cz2Trz      | −/−/−                                         | ≈505/86/3.6 (16.6 wt% in DPEPO)           | 0.18                | −5.96     | −4.16     | [47] |
| m2Cz2Trz      | −/−/−                                         | ≈510/95.6/12.2 (10 wt% in DPEPO)          | 0.09                | −5.92     | −3.33     | [47] |
| DTRZ−Di       | 506/−/−.2.48(PhMe)                            | 521/83/1.47 (25 wt% in TCTA:Bepp2)        | 0.03                | −5.68     | −2.98     | [35] |
| TRZoCz        | ≈450/−/− (PhMe)                               | −/−/20 (10% in DPEPO)                    | 0.20                | −6.03     | −3.30     | [48] |
| TRZoTzCz      | ≈480/−/− (PhMe)                               | −/−/98 (10% in DPEPO)                    | 0.06                | −5.9      | −3.17     | [48] |
TCZTRZ(Me2p) \( \lambda_{\text{PL}}: 442 \text{ nm}; \Phi_{\text{PL}}: 30\%; \tau_{d}: 39 \mu s \) (15 wt% in DPEPO); \( \Delta E_{\text{ST}}: 0.14 \text{ eV} \) and TCZTRZ(Me2o) \( \lambda_{\text{PL}}: 435 \text{ nm}; \Phi_{\text{PL}}: 17\%; \tau_{d}: 37 \mu s \) (15 wt% in DPEPO); \( \Delta E_{\text{ST}}: 0.18 \text{ eV} \) results in compounds showing a blue-shifted emission, shorter \( \tau_{d} \) and lower \( \Phi_{\text{PL}} \) than TCZTRZ(Me). The OLEDs employing TCZTRZ \( [\lambda_{\text{EL}}: 456 \text{ nm}; \text{CIE} = (0.16, 0.14)] \) and TCZTRZ(Me) \( [\lambda_{\text{EL}}: 448 \text{ nm}; \text{CIE} = (0.16, 0.14)] \) result in compounds showing a blue-shifted emission, shorter \( \tau_{d} \) and lower \( \Phi_{\text{PL}} \) than TCZTRZ(Me).
the emission in TRZ-DCF donor by incorporating a distal carbazole served to red-shift enhanced conjugation of the donors results in a higher however, the increased oscillator strength caused by the donor (\( \Phi_{PL} \)) of larger values of 0.7%, 0.9% and 2.8%, respectively. The author attributed the improved performance of those devices to the weak absorption, low \( \Phi_{PL} \), and rapid degradation of the emitters under electrical excitation.

Liao et al.\(^5\) reported two blue TADF materials TRZ-CF (\( \Phi_{PL} \) ≈ 480 nm; \( \Phi_{EL} \) = 85.9%; \( \tau_{EL} \) = 7.34 μs; \( \Delta E_{ST} \) = 0.22 eV; 20 wt% in DPEPO) and TRZ-CzF (\( \lambda_{PL} \) ≈ 460 nm; \( \Phi_{PL} \) = 68.6%; \( \tau_{PL} \) = 10.68 μs; \( \Delta E_{ST} \) = 0.31 eV; 20 wt% in DPEPO) that likewise incorporate a methyl group on the arylene bridge at a position \( o- \) to the donor (Figure 25), resembling the structure of TCZTRZ\( (Me) \). However, the increased oscillator strength caused by the enhanced conjugation of the donors results in a higher \( \Phi_{PL} \) of these two compounds compared to TCZTRZ\( (Me) \), but at a cost of larger \( \Delta E_{ST} \), indicating that the methyl group is not sufficiently bulky to induce a highly twisted structure that can result in the required separation of the FMOs. Despite the red-shifted PL spectra, the OLEDs still exhibited blue emission with \( \lambda_{EL} \) at 476 and 460 nm and EQEmax of 20% and 13.3% for the devices with TRZ-CF and TRZ-CzF, respectively. Strengthening the donor by incorporating a distal carbazole served to red-shift the emission in TRZ-DCF (\( \Phi_{PL} \) = 84%; \( \tau_{PL} \) = 5.43 μs; 20 wt% in DPEPO) while the other photophysical properties remain unchanged.\(^5\) Compared to the OLED with TRZ-CF [\( \lambda_{EL} \) = 476 nm; CIE = (0.17, 0.27)], a slightly lower EQEmax of 18.7% was obtained for the sky-blue device with TRZ-DCF [\( \lambda_{EL} \) = 484 nm; CIE = (0.20, 0.33)].

The use of a phenyl substituent on the arylene bridge was explored by Lee et al.\(^6\) to modulate the conformation of the emitter. A cross-comparison of the photophysical properties of 1PCTRZ (\( \Phi_{PL} \) = 87%; \( \tau_{PL} \) = 55.8 μs; \( \Delta E_{ST} \) = 0.16 eV; 10 wt% in DPEPO) and 2PCTRZ (\( \Phi_{PL} \) = 90%; \( \tau_{PL} \) = 31.4 μs; \( \Delta E_{ST} \) = 0.11 eV; 10 wt% in DPEPO) reveals how \( o- \) disubstitution leads to a more twisted conformation (dihedral angle for 1PCTRZ of 60.2° is smaller than that of 2PCTRZ of 68.2°), which translates into a smaller \( \Delta E_{ST} \) and a shorter \( \tau_{EL} \), but without negatively impacting \( \Phi_{PL} \). However, the donor group adopts a less twisted conformation that those of TCZTRZ\( (Me) \), TCZTRZ\( (Me2p) \) and TCZTRZ\( (Me2o) \), all of which contain methyl substituents. This suggests that the phenyl group is effectively less bulky than the methyl substituent. High EQEmax values were obtained for the OLEDs with 1PCTRZ [EQEmax = 26.7%; \( \lambda_{EL} \) = 476 nm; CIE = (0.17, 0.27)] and 2PCTRZ [EQEmax = 28.5%; \( \lambda_{EL} \) = 488 nm; CIE = (0.18, 0.35)].

Liao et al. have also explored the use of fluorine atom decoration of the phenylene bridge\(^7\) in order to explore their influence on the photophysical properties of the emitters. They found that fluoro-substitution can reduce the \( \Delta E_{ST} \) as a result of an increased dihedral angle between the bridge and the donor by cross-comparing TCTZ (\( \Phi_{PL} \) = 84%; \( \tau_{PL} \) = 10.09 μs; \( \Delta E_{ST} \) = 0.13 eV; 6 wt% in DPEPO), TCTZ-F (\( \Phi_{PL} \) = 92%; \( \tau_{PL} \) = 9.20 μs; \( \Delta E_{ST} \) = 0.10 eV; 6 wt% in DPEPO) and TCTZ-2F (\( \Phi_{PL} \) = 88%; \( \tau_{PL} \) = 6.41 μs; \( \Delta E_{ST} \) = 0.08 eV; 6 wt% in DPEPO), as shown in Figure 26. The calculated dihedral angles of the ground-state optimized structures between the tetracarbazole donor with the phenylene bridge increase slightly from 53.2°, 56.7° to 57.3° with increasing number of fluorine atoms. The minor changes to the dihedral angle are consistent with the small volume of the fluorine atoms. The strongly inductively withdrawing character of fluorine is responsible for the progressive stabilization of the \( S_1 \) state from 3.06, 2.56, to 2.90 eV for TCTZ, TCTZ-F and TCTZ-2F, respectively, while the triplet energies remain almost the same at 2.87, 2.86 to 2.85 eV, respectively. It is interesting to observe that TCTZ-F has the best balance between a small \( \Delta E_{ST} \) and reasonably high oscillator strength, which is manifested in the highest \( \Phi_{PL} \) of the three compounds. The best EQEmax was 26.7% for 1PCTRZ at 476 nm, while the EQEmax for 2PCTRZ was 28.5% at 488 nm.
achieved for the TCTZ-F-based device [EQE\textsubscript{max} = 22.5\%; \lambda\textsubscript{EL}: 500 nm; CIE = (0.24, 0.43)] compared to the devices with TCTZ [EQE\textsubscript{max} = 17.1\%; \lambda\textsubscript{EL}: 472 nm; CIE = (0.16, 0.24)] and TCTZ-2F [EQE\textsubscript{max} = 19.6\%; \lambda\textsubscript{EL}: 512 nm; CIE = (0.27, 0.46)].

Isosteric trifluoromethyl groups have also been introduced onto the arylene bridge in a series of blue TADF emitters: TRZCz-Me, TRZCz-Me-1, TRZCz-DMe, TRZCz-CF3, TRZCz-CF3-1, TRZBuCz-CF3, and TRZBuCz-CF3-1, as shown in Figure 27.\textsuperscript{[54]} Only TRZCz-CF3 (\lambda\textsubscript{PL}: 465 nm; \Phi\textsubscript{PL}: 27.8\%; \tau\textsubscript{d}: 5.62 \mu s in 5 wt% in mCP; \Delta E\textsubscript{ST}: 0.05 eV) and TRZBuCz-CF3 (\lambda\textsubscript{PL}: 476 nm; \Phi\textsubscript{PL}: 31.8\%; in 10 wt% in mCP; \Delta E\textsubscript{ST}: 0.35 eV) with methyl groups similarly ortho-disposed to carbazole are not TADF emitters, while similar analogs TRZ-CF3 and TRZ-CzF with different donor structures to the above work demonstrated TADF. The \Phi\textsubscript{PL} was not completely dependent on the position of substituent groups on the bridge, for example, as evidenced by the large deviation between TRZCz-CF3-1 (\Phi\textsubscript{PL} 48\%) and TRZBuCz-CF3-1 (\Phi\textsubscript{PL} 99\%), the latter of which also contains a more strongly electron-donating 3,6-ditert-butylcarbazole donor. The blue OLEDs fabricated with TRZCz-CF3 and TRZBuCz-CF3 achieved EQE\textsubscript{max} of 9.4\% and 14.2\% with CIE coordinates of (0.19, 0.23) and (0.18, 0.29), respectively.

Another strong electron-withdrawing group, CN, was used in lieu of the trifluoromethyl groups in a series of emitters reported by Hong et al. (Figure 27).\textsuperscript{[55]} Compared to TRZCz-CF3, CzCNTRZ (\lambda\textsubscript{PL}: 458 nm; \Phi\textsubscript{PL}: 46\%; \tau\textsubscript{d}: 47.9 \mu s; \Delta E\textsubscript{ST}: 0.21 eV; 10 wt% in DPEPO) shows a slightly more prominent and improved \Phi\textsubscript{PL} at the cost of a larger \Delta E\textsubscript{ST} of 0.21 eV. The similar emission was attributed to the identical electron-withdrawing ability of the two electron-withdrawing groups; however, the larger \Delta E\textsubscript{ST} is indicative of a smaller steric bulk from the CN substituent. Thanks to the higher \Phi\textsubscript{PL}, the EQE\textsubscript{max} of the CzCNTRZ-based device reached 13.9\%. Similar to the PL spectrum, the CzCNTRZ device showed blue (\lambda\textsubscript{EL} = 461 nm) emission with CIE coordinates of (0.15, 0.16), which resembles the emission profile of the TRZCz-CF3 device (\lambda\textsubscript{EL} = 464 nm).

Hong et al.\textsuperscript{[56]} also examined the effect of incorporation of a CN unit acting as a secondary electron acceptor on the TADF properties (Figure 27). The addition of the nitrile intensified the CT character of the emitters due to the enhanced acceptor strength, evidenced by the red-shifted emission spectrum. Compared to TRZBFcCz (\Phi\textsubscript{PL}: 99.8\%; \tau\textsubscript{d}: 26.3 \mu s in 10 wt% in DPEPO; \Delta E\textsubscript{ST}: 0.27 eV), the \Delta E\textsubscript{ST} is reduced yet the \Phi\textsubscript{PL} is maintained at 100\% in TRZCNBFcCz (\Phi\textsubscript{PL}: 100\%; \tau\textsubscript{d}: 9.4 \mu s in 10 wt% in DPEPO; \Delta E\textsubscript{ST}: 0.13 eV), enabling a high EQE\textsubscript{max} of 26.6\% in the sky-blue TADF OLED (\lambda\textsubscript{EL}: 481 nm). However, the addition of two CN substituents in TRZ2CNBFcCz resulted in both a lower \Phi\textsubscript{PL} of 62\% and a smaller \Delta E\textsubscript{ST} of 0.1 eV (\Phi\textsubscript{PL}: 62\%; \tau\textsubscript{d}: 31 \mu s in Figure 27. Molecular structures and properties of TRZ-based TADF emitters with modification to the phenylene bridge.
10 wt% in DPEPO; $\Delta E_{ST}$: 0.1 eV), producing a green device ($\lambda_{EL}: 511$ nm) with a lower EQE$_{max}$ of 15.8%. The OLED with the control compound TRZBFCz that does not have any CN groups on the triazine bridge showed an EQE$_{max}$ of 19% and a $\lambda_{EL}$ of 447 nm with color coordinates of (0.15, 0.09).

Lee et al.$^{[5]7}$ reported dBFCzTRZ ($\lambda_{PL}: 420$ nm; $\Phi_{PL}: 90$%; $\tau_d$: 30.4 $\mu$s; $\Delta E_{ST}$: 0.13 eV; 20 wt% in DPEPO) and dBFCzCNTRZ ($\lambda_{PL}: 490$ nm; $\Phi_{PL}: 81$%; $\tau_d$: 4.9 $\mu$s; $\Delta E_{ST}$: 0.09 eV; 20 wt% in DPEPO) that each employ a more conjugated donor and where the only difference between the two comes from the inclusion of the CN group on the phenylene bridge in dBFCzCNTRZ (Figure 27). Calculations showed that the HOMOs of both dBFCzTRZ ($-5.25$ eV) and dBFCzCNTRZ ($-5.40$ eV) are mainly localized on the donor moiety, while the LUMOs of dBFCzTRZ ($-2.78$ eV) and dBFCzCNTRZ ($-3.06$ eV) are distributed on both the aryne linker and the triazine acceptor. The CN unit in dBFCzCNTRZ promotes a stabilization of both the HOMO and LUMO levels, but the LUMO more pronounced. The dihedral angles between the donor moiety and the aryne bridge in dBFCzCNTRZ and dBFCzTRZ are similar at 75.1° and 71.1°, respectively, indicating the negligible steric influence from the nitrile. The $S_1/T_1$ energies of dBFCzCNTRZ (2.97/2.88 eV) are both more stabilized than those of dBFCzTRZ (3.15/3.02 eV). Despite the similar $\Delta E_{ST}$, the $\tau_d$ for dBFCzCNTRZ is much faster at 4.9 $\mu$s compared to 30.4 $\mu$s for dBFCzTRZ. There is a small sacrifice in $\Phi_{PL}$ of 81% for dBFCzCNTRZ compared to 90% for dBFCzTRZ. The OLEDs based on dBFCzCNTRZ and dBFCzTRZ demonstrated high EQE$_{max}$ of 27.5% and 22.6%, respectively. dBFCzCNTRZ with the lower $\Phi_{PL}$, however, produced a higher efficiency device which may be attributed to the better electron mobility resulting from the presence of the nitrile group. The operational lifetime ($LT_{80}$), defined as the lifetime of the device to reach 80% of its initial luminance, of the dBFCzCNTRZ device [$\lambda_{EL}: 497$ nm; $LT_{80}: \approx 36$ h; CIE $= (0.22, 0.47)$] was over three times longer than that of the dBFCzTRZ device [$\lambda_{EL}: 476$ nm; $LT_{80}: \approx 11$ h; CIE $= (0.16, 0.27)$]. The high $k_{TISC}$ of the dBFCzCNTRZ emitter contributed to the enhanced device lifetime by suppressing triplet exciton triggered degradation mechanisms. The photophysical and electrochemical characteristics of the aforementioned materials are summarized in Table 11, and representative device performance is summarized in Table 12.

Table 11. Summary of photophysical and electrochemical properties.

| Emitter | Solution $\lambda$/$\Phi$/$\tau$ (medium) | Solid State $\lambda$/$\Phi$/$\tau$ (medium) | $\Delta E_{ST}$ | HOMO | LUMO | Ref. |
|---------|------------------------------------------|-------------------------------------------|----------------|-------|-------|------|
| TCZ – TRZ | 432/77/— (PhMe) | 457/40/38 (15 wt% in DPEPO) | 0.27 | —6.54 | —5.27 | [112] |
| TCZ – TRZ(Me) | 431/60/— (PhMe) | 451/32/51 (15 wt% in DPEPO) | 0.16 | —5.64 | —5.54 | [112] |
| TCZ – TRZ(Me') | 429/80/— (PhMe) | 444/51/58 (15 wt% in DPEPO) | 0.12 | —5.60 | —5.52 | [112] |
| TCZ – TRZ(Me2p) | 427/46/— (PhMe) | 442/30/39 (15 wt% in DPEPO) | 0.14 | —5.62 | —2.46 | [112] |
| TCZ – TRZ(Me2o) | 427/47/— (PhMe) | 435/17/37 (15 wt% in DPEPO) | 0.18 | —5.39 | —2.33 | [112] |
| TRZ – CF | 452/—/— (PhMe) | ≈480/85.9/7.34 (20 wt% in DPEPO) | 0.22 | —5.34 | —2.37 | [50] |
| TRZ – CsF | 445/—/— (PhMe) | ≈460/68.6/10.68 (20 wt% in DPEPO) | 0.31 | —5.47 | —2.42 | [50] |
| TRZ – DCF | 454/—/— (PhMe) | —84/5.43 (20 wt% in DPEPO) | 0.22 | —5.36 | —2.34 | [51] |
| 1PCTrz | —/—/— | —87/55.8 (10 wt% in DPEPO) | 0.16 | —5.49 | —2.51 | [52] |
| 2PCTrz | —/—/— | —90/11.4 (10 wt% in DPEPO) | 0.11 | —5.50 | —2.45 | [52] |
| TCTZ | 444/—/— (PhMe) | —84/10.09 (6 wt% in DPEPO) | 0.13 | —5.68 | —2.27 | [53] |
| TCTZ – F | 465/—/— (PhMe) | —/29/20 (6 wt% in DPEPO) | 0.10 | —5.68 | —2.40 | [53] |
| TCTZ – 2 F | 489/—/— (PhMe) | —88/6.41 (6 wt% in DPEPO) | 0.08 | —5.68 | —2.51 | [53] |
| TrzCz – Me | 414/—/— (PhMe) | 435/57.5/— (10 wt% in DPEPO) | 0.36 | —5.66 | —2.92 | [54] |
| TrzCz – Me – 1 | 414/—/— (PhMe) | 435/73/— (10 wt% in DPEPO) | 0.35 | —5.64 | —2.94 | [54] |
| TrzCz – Dme | 414/—/— (PhMe) | 434/31.8/— (10 wt% in DPEPO) | 0.35 | —5.66 | —2.90 | [54] |
| TrzCz – CF3 | 457/—/— (PhMe) | 465/27.8/5.62 (5 wt% in mCP) | 0.05 | —5.76 | —3.10 | [54] |
| TrzCz – CF3 – 1 | 443/—/— (PhMe) | 450/48.1/— (5 wt% in mCP) | 0.24 | —5.73 | —3.05 | [54] |
| TrzBuCz – CF3 | 476/—/— (PhMe) | 476/72/6.3 (5 wt% in mCP) | 0.02 | —5.61 | —3.12 | [54] |
| TrzBuCz – CF3 – 1 | 466/—/— (PhMe) | 466/99/— (5 wt% in mCP) | 0.14 | —5.60 | —3.06 | [54] |
| TrzBF7Cz | ≈400/—/— (THF) | —99/8/26.3 (10 wt% in DPEPO) | 0.27 | —6.04 | —3.21 | [56] |
| TrzCNBF7Cz | ≈450/—/— (THF) | —/100/9.4 (10 wt% in DPEPO) | 0.13 | —6.16 | —3.41 | [56] |
| Trz2CNBF7Cz | ≈510/—/— (THF) | —/62/3.1 (10 wt% in DPEPO) | 0.10 | —6.37 | —4.08 | [56] |
| CzCNTrz | —/—/— | 458/46/47.9 (10 wt% in DPEPO) | 0.21 | —6.27 | —3.24 | [55] |
| dBFCzCNTrz | —/—/— | —/81/4.9 (20 wt% in DPEPO) | 0.09 | —6.17 | —3.06 | [57] |
| dBFCzTrz | —/—/— | —/0.9/30.4 (20 wt% in DPEPO) | 0.13 | —6.17 | —2.78 | [57] |
Table 12. Summary of device structures and performance.

| Emitter   | Device Structure                     | $E_{\text{Lmax}}$ [nm] | CIE     | $V_{\text{on}}$ [V] | EQE/PE/CE [%/lm W$^{-1}$/cd A$^{-1}$] | EQE100/1000 [cd/m$^2$] | Ref. |
|-----------|--------------------------------------|-------------------------|---------|-------------------|--------------------------------------|-------------------------|------|
| TCZ–TRZ   | ITO/HAT– CN/NPB/mCP/DPEPO: 15 wt%/emitter/PPF/PFF/LiQ/LiQ/Al | 456 (0.159, 0.142) 3.8 | 10.4/–/11.6 | N/A                | [112]                      |
| TCZ–TRZ(Me) | ITO/HAT– CN/NPB/mCP/DPEPO: 15 wt%/emitter/PPF/PFF/LiQ/LiQ/Al | 448 (0.170, 0.179) 4  | 11.1/–/12.8 | N/A                | [112]                      |
| TCZ–TRZ(Me$^*$) | ITO/HAT– CN/NPB/mCP/DPEPO: 15 wt%/emitter/PPF/PFF/LiQ/LiQ/Al | 450 (0.203, 0.229) 4.4 | 0.7/–/1.0  | N/A                | [112]                      |
| TCZ–TRZ(Me2p) | ITO/HAT– CN/NPB/mCP/DPEPO: 15 wt%/emitter/PPF/PFF/LiQ/LiQ/Al | 447 (0.197, 0.214) 5 | 0.9/–/1.0  | N/A                | [112]                      |
| TCZ–TRZ(Me2o) | ITO/HAT– CN/NPB/mCP/DPEPO: 15 wt%/emitter/PPF/PFF/LiQ/LiQ/Al | 444 (0.228, 0.289) 4.6 | 2.8/–/2.7  | N/A                | [112]                      |
| TRZ–CF    | ITO/HATCN/TAPC/TCTA/mCP/DPEPO: 20 wt%TRZ– CF/DPEPO/TmPyPB/LiQ/Al | 476 (0.17, 0.27) 2.9 | 20/28/36  | ≈15/[11.4]        | [50]                      |
| TRZ–CzF   | ITO/HATCN/TAPC/TCTA/mCP/DPEPO: 20 wt%TRZ– CzF/DPEPO/TmPyPB/LiQ/Al | 460 (0.15, 0.16) 3.5 | 13.3/10.7/16.5 | ≈6.0/[3.7]        | [50]                      |
| TRZ–DCF   | ITO/HAT– CN/TAPC/mCP/DPEPO: TRZ– DCF 20%/DPEPO/TmPyPB/LiQ/Al | 484 (0.20, 0.33) 3.5 | 20/35/53.9 | ≈18.0/[15]        | [51]                      |
| 1PCTrz    | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:20%/TSPO1/TPB/LiQ/A | 482 (0.17, 0.30) 6   | 26.7/–     | ≈15.0/[11.7]       | [52]                      |
| 2PCTrz    | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:20%/TSPO1/TPB/LiQ/A | 488 (0.18, 0.35) 6   | 28.5/–     | ≈22.0/[19.4]       | [52]                      |
| TCTZ      | ITO/HAT– CN/TAPC/mCP/DPEPO:6%/TCTZ-3TYPYMB/LiQ/Al | 472 (0.16, 0.24) 4.5 | 17.1/19.7/28.0 | –/8.6            | [53]                      |
| TCTZ–F    | ITO/HAT– CN/TAPC/mCP/DPEPO:6%/TCTZ–F/3TYPYMB/LiQ/Al | 500 (0.24, 0.43) 4.4 | 22.5/40.8/56.5 | –/16.2           | [53]                      |
| TCTZ–2F   | ITO/HAT– CN/TAPC/mCP/DPEPO:6%/TCTZ–2F/3TYPYMB/LiQ/Al | 512 (0.27, 0.46) 4.7 | 19.6/35.1/32.5 | –/14.9           | [53]                      |
| TrzCz–Me  | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 434 (0.16, 0.08) 4.3 | 4.8/2.51/3.44 | N/A               | [54]                      |
| TrzCz–Me1 | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 434 (0.16, 0.08) 4.8 | 3.3/1.65/2.52 | N/A               | [54]                      |
| TrzCz–Dme | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 436 (0.16, 0.09) 4.3 | 3.19/1.35/2.48 | N/A               | [54]                      |
| TrzCz–CF3 | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 464 (0.19, 0.23) 3.9 | 9.4/12.83/15.92 | N/A               | [54]                      |
| TrzCz–CF3–1 | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 448 (0.17, 0.15) 3.9 | 7.17/12.7/15.8 | N/A               | [54]                      |
| TrzBuCz–CF3 | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 472 (0.18, 0.29) 4.1 | 14.22/19.5/26.7 | N/A               | [54]                      |
| TrzBuCz–CF3–1 | ITO/PEDOT-PSS/NPB/mCP/TCTA/DPEPO:10%emer/TmPyPB/LiQ/A | 452 (0.17, 0.16) 3.9 | 7.97/14.19/17.88 | N/A               | [54]                      |
| TrzBFCz   | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:10%TrzBFCz/TSPO1/TPB/LiQ/A | 447 (0.15, 0.09) 8.1 | 19/–/–     | ≈6.0/[4.3]        | [56]                      |
| TrzCNBFCz | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:20%TrzBFCz/TSPO1/TPB/LiQ/A | 481 (0.17, 0.31) 6.5 | 26.6/–/–    | ≈22.0/[16.8]      | [56]                      |
| Trz2CNBFCz | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:10%TrzBFCz/TSPO1/TPB/LiQ/A | 511 (0.27, 0.52) 9  | 15.8/–/–    | ≈14/[6.9]        | [56]                      |
| CcCNTrz   | ITO/PEDOT-PSS/TAPC/mCP/EML (25 nm:10 wt%) | 461 (0.15, 0.16) 6   | 13.9/18.3/18.3 | 9.5/≈2.0      | [55]                      |
| dBFCcCNTrz | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:emitters/TSPO1/TPB/LiQ/A | 497 (0.22, 0.47) 5.2 | 27.5/–/–    | ≈26.0/[24.3]     | [57]                      |
| dBFCcTrz  | ITO/PEDOT-PSS/TAPC/mCP/DPEPO:emitters/TSPO1/TPB/LiQ/A | 476 (0.16, 0.27) 5.6 | 22.6/–/–    | ≈17.0/[12.3]     | [57]                      |
8. Functionalization of the Triazine

Lee et al.\[58\] developed a blue TADF emitter, mtCzTRZ ($\lambda_{PL}$: 469 nm; $\Phi_{PL}$: 65%; $\tau_{D}$: 118.6 $\mu$s in 1 wt% in PS; $\Delta E_{ST}$: 0.06 eV), by attaching a para-methoxy group to one of the phenyl rings of the TRZ acceptor, which was designed to blue shift the emission compared to tCzTRZ by weakening its electron-withdrawing capacity (Figure 28). The control compound, tCzTRZ ($\lambda_{PL}$: 469 nm; $\Phi_{PL}$: 67%; $\tau_{D}$: 89.4 $\mu$s in 1 wt% in PS; $\Delta E_{ST}$: 0.05 eV), showed identical PL and similar photophysical properties to that of mtCzTRZ, indicating that there is negligible influence of the photophysical properties due to the presence of the methoxy group on the TRZ acceptor. However, the modification resulted in an improvement in the device performance. The solution-processed OLED with mtCzTRZ dispersed into the (5-((tert-butyl)-2-(4-((tert-butyl)phenoxy)phenyl)diphenylphosphine oxide (POBBPE)\[59\] host as the emitting layer, a more soluble analog to the PL maximum of $\lambda_{EL}$ of 450 nm, which though not directly comparable is 0.22 eV), also developed by Lee et al.,\[60\] is an emitter containing a triazine acceptor with an inductively electron-withdrawing para-fluoro group onto one of the phenyl rings of the TRZ (Figure 28). 3,6-Di-tert-butylcarbazole groups connected at the ortho positions of the other two phenyl rings complete the donor–acceptor structure. Their placement was to prevent intermolecular interactions, a similar strategy to that used in o-CzTRZ (Figure 4). FTRZTCz showed a PL spectrum in toluene with the maximum at 455 nm, which though not directly comparable is similar to the PL maximum of o-CzTRZ ($\lambda_{PL}$: 455 nm, 5 wt% in mCP) in mCP matrix. The missing information related to the compound without the fluoro group makes it difficult to conclude how much the fluoro substituent contributes to the shift of the PL given the similar donor-ortho-acceptor skeleton. However, it is still possible to infer the influence of the fluoro group by comparing the properties of the compound with the previously reported molecule o-CzTRZ, which only has one ortho-connected carbazole. The red-shifted EL for the device with FTRZTCz ($\lambda_{EL}$: 496 nm, CIE coordinates of (0.20, 0.45)) compared to that with o-CzTRZ ($\lambda_{EL}$: 470 nm, CIE: (0.15, 0.22)) reveals the presence of a stronger electron-accepting triazine derivative in FTRZTCz compared to o-CzTRZ.

Xu et al.\[61\] employed diphenylphosphine oxide (PO) as secondary acceptors within a series of D–A–A-type TADF emitters with the collective name of txBCzPO3-nTPTZ ($x = o, m,$ and $p$, corresponding to placement of the diphenylphosphine oxide at the ortho-, meta-, and para-positions; and $n = 1$ and 2, corresponding to the number of diphenylphosphine oxide acceptors), in which tBCz is 3,6-di-tert-butylcarbazole, and TPTZ is triphenyltriazine (aka TRZ) as shown in Figure 29. The incorporation of the electron-withdrawing PO group serves to stabilize the excited states and to enhance the CT character, leading to a greater localization of the FMO distributions. By virtue of this design strategy, ptBCzPO2TPTZ (o-CzTRZ: $\lambda_{PL}$: 494 nm; $\Phi_{PL}$: 96%; in 10 wt% in DPEPO; $\Delta E_{ST}$: 0.01 eV) as the best example among this series, has almost unity $\Phi_{PL}$ (96%) and very efficient RISC efficiency, $\Phi_{RISC}$, of 98% and $k_{RISC}$ of 5.42 $\times$ 10$^4$. These properties established the basis for the high-performance OLED, which showed an EQE$\text{max}$ of 28.9% at $\lambda_{EL}$ of 492 nm, corresponding to CIE coordinates of (0.18, 0.42). It is worth noting that the analog p-CzTRZ (Figure 4) without the PO groups does not show any TADF properties due to its too large $\Delta E_{ST}$ of 0.36 eV in 10 wt% in DPEPO. The other derivatives in this work showed moderate $\Phi_{PL}$s ranging from 38% to 74%. The photophysical and electrochemical data of the aforementioned materials are summarized in Table 13, and representative device performance is summarized in Table 14.

9. Intramolecular Through Space Charge Transfer (TSCT) of Triazine Based TADF Emitters

The prior examples have implicated an $S_1$ state that has CT character and that the charge transfer process is mediated by...
a π-conjugated bridging moiety. This type of CT is termed TBCT.\[^{[62]}\] There exists a second CT process that is mediated by π-stacking of the donor and acceptor units, termed through-space charge transfer (TSCT). Distinct from most of the TBCT emitters that feature strong electron coupling through covalent bonds, TSCT emitters possess weaker electronic interaction between donors and acceptors due to the relatively smaller overlap of the FMOs in these systems. The degree of electronic coupling is controlled by the distance and the relative angles between the donor and acceptor groups. For example, an

Figure 29. Molecular structures and properties of TADF emitters based on diphenylphosphine oxide (PO) functionalized triazine.

Table 13. Summary of photophysical and electrochemical properties.

| Emitter     | Solution λ\textsubscript{PL}/Φ\textsubscript{PL}/τ\textsubscript{PL} (medium) [nm/%/μs] | Solid State λ\textsubscript{PL}/Φ\textsubscript{PL}/τ\textsubscript{PL} (medium) [nm/%/μs] | ΔE\textsubscript{ST} [eV] | HOMO [eV] | LUMO [eV] | Ref. |
|-------------|----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|-----------------|-------|-------|-------|
| mtCzTrz     | 469/118.6 (1 wt% in PS)                                                                                       | 488/45.1 (1 wt% in PS)                                                                       | 0.06            | −6.08 | −3.41 | [58] |
| tCzTrz      | 469/118.6 (1 wt% in PS)                                                                                       | 488/45.1 (1 wt% in PS)                                                                       | 0.05            | −6.09 | −3.43 | [58] |
| ptBCzPO2TPTZ| 506/96 (10 wt% in DPEPO)                                                                                      | 504/96 (10 wt% in DPEPO)                                                                     | 0.01            | −6.05 | −3.60 | [61] |
| otBCzPO2TPTZ| 518/118.6 (10 wt% in DPEPO)                                                                                    | 504/96 (10 wt% in DPEPO)                                                                     | 0.03            | −6.04 | −3.48 | [61] |
| ntBCzPO2TPTZ| 512/72 (10 wt% in DPEPO)                                                                                        | 484/72 (10 wt% in DPEPO)                                                                     | 0.02            | −6.08 | −3.60 | [61] |
| mtBCzPO2TPTZ| 506/118.6 (10 wt% in DPEPO)                                                                                    | 494/96 (10 wt% in DPEPO)                                                                     | 0.01            | −6.05 | −3.60 | [61] |
| otBCz2POTPTZ| 514/118.6 (10 wt% in DPEPO)                                                                                    | 504/96 (10 wt% in DPEPO)                                                                     | 0.01            | −6.05 | −3.53 | [61] |
| ntBCz2POTPTZ| 514/118.6 (10 wt% in DPEPO)                                                                                    | 484/72 (10 wt% in DPEPO)                                                                     | 0.02            | −6.08 | −3.58 | [61] |
| ptBCz2POTPTZ| 496/72 (10 wt% in DPEPO)                                                                                        | 494/96 (10 wt% in DPEPO)                                                                     | 0.01            | −6.04 | −3.50 | [61] |
| FTrzTCz     | 450/5.91 (10% in DPEPO)                                                                                        | −85/5.91 (10% in DPEPO)                                                                      | 0.22            | −6.13 | −3.42 | [60] |
orth-substitution pattern between the donor and acceptor moieties leads to sterically congested, co-facially aligned donor and acceptor groups in the molecule, inducing either a π−π* type (as in the B-oTC emitter) or an n−π* type (as in TRZ-oCz) interaction. The conformationally restricted structures result in limited change in the geometry of the emitter in the excited states and small reorganization energies, reflected in the narrower emission profiles of these compounds.

Swager et al. reported a series of TADF emitters possessing a TSCT state. As shown in Figure 29, the design of XPT, XCT, and XBUtCT is based on a xanthene scaffold with a donor and an acceptor co-facially aligned at a well-defined distance. These compounds possess very small ΔEST values as evidenced by DFT calculation (Figure 30), and the close alignment between the donor and acceptor groups restricts motion in the solid state, resulting in aggregation induced delayed fluorescence (AIDF) as exemplified by the increase in ΦPL from dilute toluene to 10 wt% DPEPO films of XPT and XBUtCT [XPT (ΦPL: 7.7% in toluene, ΦPL: 66% in 10 wt% in DPEPO), and XBUtCT (ΦPL: 6.0% in toluene, ΦPL: 35% in 10 wt% in DPEPO)]. The strength of the electron donor directly impacted the corresponding emission color of the emitters as evidenced by the PL maximum shifting from 419 nm in XCT to 451 nm in XPT and 562 nm in XBUtCT. The OLED with XPT showed a 10% EQEmax with λEL at 386 nm while XBUtCT-based device exhibited a 4% EQEmax (limited by its lower ΦPL) with λEL at 488 nm.

Lee et al. found that ortho-linked donor and acceptor compounds showed superior TADF properties to those where the donor was either meta- or para-disposed. The authors compared the optoelectronic properties of oBFCzTRZ, mBFCzTRZ, and pBFCzTRZ, which are based on ortho-, meta-, and para-linked diphenyltriazine and benzofurocarbazole groups (Figure 31). It is noteworthy that the ΔEST of oBFCzTRZ is only 0.002 eV, while those of mBFCzTRZ and pBFCzTRZ are 0.191 and 0.302 eV, respectively, revealing the much weaker electronic coupling within the former. Moreover, oBFCzTRZ (ΦPL: 97.9%; τEL: 5.4 μs in 10 wt% in DPEPO) also possessed a shorter delayed lifetime, and higher ΦPL than mBFCzTRZ (ΦPL: 31.1%; τEL: 29.6 μs in 10 wt% in DPEPO) and pBFCzTRZ (ΦPL: 85.3%; τEL: 31.2 μs in 10 wt% in DPEPO), reflective of the more efficient RISC process in the former. The higher ΦPL is likely due to the suppression of nonradiative decay due to the more conformationally restricted structure in oBFCzTRZ. Blue-emitting devices with oBFCzTRZ (λEL = 477 nm) > mBFCzTRZ (λEL = 473 nm) > pBFCzTRZ (λEL = 465 nm) showed EQEmax of 20.4% [EQEmax: 477 nm; CIE = (0.18, 0.31)], 13.2% [EQEmax: 473 nm; CIE = (0.17, 0.25)], and 16.7% [EQEmax: 465 nm; CIE = (0.15, 0.18)], respectively. Importantly, oBFCzTRZ-based device showed the least amount of efficiency roll-off.

Expanding on the ortho-disposed donor–acceptor platform, Lee et al. reported green TADF emitters DPA-oTRZ and MPA-oTRZ (Figure 31), which incorporated a diphenylamine group whose electron donating ability is stronger than benzofurocarbazole as in oBFCzTRZ. Thus, both DPA-oTRZ and MPA-oTRZ exhibited red-shifted PL with λPL at around 500 and 530 nm, respectively. Similar to the other TSCT emitters, DPA-oTRZ and MPA-oTRZ also have very small ΔEST values of 0.03 and 0.01 eV, respectively, and comparatively short delayed lifetimes of 1.62 μs and 1.08 μs, respectively. The OLEDs based on DPA-oTRZ [EQEmax: 497 nm; CIE = (0.21, 0.45)] and MPA-oTRZ [EQEmax: 532 nm; CIE = (0.35, 0.58)] showed EQEmax of 17.2% and 16.3%.

Using DFT calculations, Bredas et al. investigated the origins of the TSCT in a number of TADF emitters (Figure 32). Two pathways for TSCT were identified:

### Table 14. Summary of device structures and performance.

| Emitter | Device Structure | ELmax [nm] | CIE | V_on [V] | EQE/PE/CE [%] | EQE100/1000 [cd/m²] | Ref. |
|---------|-----------------|------------|-----|----------|---------------|-----------------------|-----|
| mBFCzTRz | ITO/PEDOT:PSS/PVK/POBBPE:20 wt% mBFCzTRz/ITO/PEDOT:PSS/LIF/AI | 461 | 0.16, 0.20 | 7.6 | 16.1/9.2/25 | N/A | [58] |
| tCzTrz | ITO/PEDOT:PSS/PVK/POBBPE:20 wt% tCzTrz/ITO/PEDOT:PSS/LIF/Al | 467 | 0.16, 0.24 | 8 | 12.5/7.9/21.4 | N/A | [58] |
| ptBFCzPO2TPTZ | ITO/MoO3/mCP/80 wt% ptBFCzPO2TPTZ: DPEPO/pTPOTZ/LIF/Al | ~488 | (0.18, 0.42) | – | 28.9/79.3/73.2 | 26.1/16.4 | [61] |
| otBFCzPO2TPTZ | ITO/MoO3/mCP/80 wt% otBFCzPO2TPTZ: DPEPO/pTPOTZ/LIF/Al | 492 | (0.21, 0.46) | 3.6 | 8.1/15.8/21.9 | 8.0/7.2 | [61] |
| mBFCzPO2TPTZ | ITO/MoO3/mCP/80 wt% mBFCzPO2TPTZ: DPEPO/pTPOTZ/LIF/Al | 488 | (0.18, 0.36) | 3.2 | 17/34.6/39.7 | 12.4/5.6 | [61] |
| ptBFCzPO2TPTZ | ITO/MoO3/mCP/80 wt% ptBFCzPO2TPTZ: DPEPO/pTPOTZ/LIF/Al | 492 | (0.18, 0.42) | 2.9 | 28.9/79.3/73.2 | 26.1/16.4 | [61] |
| otBc2POTPTZ | ITO/MoO3/mCP/80 wt% otBc2POTPTZ: DPEPO/pTPOTZ/LIF/Al | 492 | (0.20, 0.44) | 2.9 | 9.3/26.5/24.5 | 7.7/6.6 | [61] |
| mBc2POTPTZ | ITO/MoO3/mCP/80 wt% mBc2POTPTZ: DPEPO/pTPOTZ/LIF/Al | 488 | (0.18, 0.37) | 3 | 10.6/22.7/24.9 | 9.0/5.0 | [61] |
| ptBc2POTPTZ | ITO/MoO3/mCP/80 wt% ptBc2POTPTZ: DPEPO/pTPOTZ/LIF/Al | 488 | (0.17, 0.32) | 2.9 | 14.9/31.7/31.9 | 14.0/9.4 | [61] |
| FTrzTCz | ITO/PEDOT:PSS/TAPC/mCP/DEPEO:20% FTrzTCz/ITO/PEDOT:PSS/LIF/Al | 496 | (0.20, 0.45) | – | 18.5/–/– | ~17.0/14.5 | [60] |
intramolecular \( \pi \cdots \pi \) and \( n \cdots \pi \) noncovalent interactions. The mechanism of the \( \pi \cdots \pi \) interaction is the one that is operational for XPT, XCT, and XtBuCT.\(^{[63]}\) However, in the cases of TRZ-oCz\(^{[17]}\) and TRZ-oBFCz, the computations indicated a very close packing between one of the nitrogen atoms of the triazine ring with the carbazole plane, which the authors asserted triggered noncovalent interactions between the lone-pair electrons of this triazine nitrogen atom and the carbazole \( \pi \) electrons. The \( n \rightarrow \pi^* \) interactions were identified as critical for enhancing the singlet–triplet spin–orbit coupling, and as a result, greatly facilitating the RISC process.

Further examples based on an ortho-connection strategy include the incorporation of a dibenzofuran as the bridge in BCzTRZDBF, TCzTRZDBF, and IDCzTRZDBF (Figure 33).

Figure 30. HOMO and LUMO orbital distributions and calculated bandgaps, singlet (\( S_1 \)), triplet (\( T_1 \)) energy levels, and oscillator strengths (\( f \)) for XPT, XCT, and XtBuCT based on TD-DFT at the B3LYP functional and 6-31 G* basis set. Reproduced with permission.\(^{[63]}\) Copyright 2017, American Chemical Society.
where substitution next to the oxygen of the dibenzofuran induced a large conformational distortion. This, coupled with the ortho-connection between the donor and acceptor, leads to shortened delayed lifetimes and small $\Delta E_{ST}$, both of which were ascribed to the TSCT character of the emissive excited state. BCzTRZDBF, TCzTRZDBF, and IDCzTRZDBF possess small $\Delta E_{ST}$ of less than 0.1 eV yet with high $\Phi_{PL}$ of 82.4, 86.3, and 85.4%, respectively, as 5 wt% in mCBPTRZ films. The best device was obtained with TCzTRZDBF as the emitter and showed an EQE of 22.4% [$\lambda_{EL}$: 496 nm; CIE $=(0.23, 0.47)$]. The devices with SF23oTz [$\Phi_{PL}$: 86% in 10 wt% in DPEPO; $\Delta E_{ST}$: 0.08 eV] and SF12oTz ($\Phi_{PL}$: 92% in 10 wt% in DPEPO; $\Delta E_{ST}$: 0.05 eV) exhibit higher TBCT contributions, with the ratio increasing to 21% and 32%, respectively. The higher TBCT contribution in SF12oTz leads to much higher ratio of delayed fluorescence (79.1% vs 39.2%) compared with SF23oTz, which the authors asserted was due to the more effective channel of TBCT over TSCT to realize charge transfer from donors to the acceptor. However, the largest $\Delta E_{ST}$ of 0.29 eV for SF34oTz in the series does not align with the expectation that a compound with a greater TSCT contribution should have the smallest $\Delta E_{ST}$ in theory. Among the three emitters, the OLED with SF12oTz performed the best, showing an EQE of 22.4% [$\lambda_{EL}$: 496 nm; CIE $=(0.23, 0.47)$]. The devices with SF23oTz [$\lambda_{EL}$: 484 nm; CIE $=(0.19, 0.35)$] and SF34oTz [$\lambda_{EL}$: 482 nm; CIE $=(0.18, 0.37)$] showed EQE of 19.6% and 14.6%, respectively. The trend in device efficiencies align with that of the $\Phi_{PL}$.
Many OLEDs that contain TADF compounds that emit from an excited state containing some TSCT character still suffer from low device performance. Recently, Kaji et al. and Liao et al. elucidated the importance of the relative orientation of donor and acceptor groups on the electronic coupling between the two in TSCT compounds that influences the magnitude of the nonradiative decay. Similar to the other TSCT molecules discussed in this section, DM-B (Φ\textsubscript{PL:} 96% in 20 wt% in DPEPO; ΔE\textsubscript{ST:} 0.17 eV) and DM-Bm (Φ\textsubscript{PL:} 92% in 20 wt% in DPEPO; ΔE\textsubscript{ST:} −0.08 eV) were designed by connecting the donor and acceptor units via a rigid fluorene linker thereby confining them into a closely packed coplanar configuration (Figure 34). DM-G (Φ\textsubscript{PL:} 88% in 20 wt% in DPEPO; ΔE\textsubscript{ST:} −0.11 eV) features a diphenyltriazine acceptor instead of triphenyltriazine in DM-B and DM-Bm. By contrast, the authors also developed a more flexible control compound DM-X (Φ\textsubscript{PL:} 32% in 20 wt% in DPEPO; ΔE\textsubscript{ST:} 0.03 eV), which differs from DM-G as it contains less rotationally constrained 1,2-phenylene bridge instead of the rigid fluorene linker. Another control compound DM-Z (Φ\textsubscript{PL:} 23% in 20 wt% in DPEPO; ΔE\textsubscript{ST:} 0.54 eV) has also been designed to analyze the effect of increasing the D/A separation by placing the donor and acceptor units on the opposite sides of the rigid fluorene linker. Despite their similar absorption and emission spectra, the Φ\textsubscript{PL values of the rigid DM-B, DM-Bm, and DM-G are remarkably higher than those of the flexible control compounds, which further validated the design strategy on the suppression of intramolecular vibrations and rotations. The ΔE\textsubscript{ST} values are 0.17, −0.08, −0.11, 0.03, and 0.54 eV for DM-B, DM-Bm, DM-G, DM-X, and DM-Z, respectively. The negative ΔE\textsubscript{ST} of DM-Bm and DM-G were attributed by the authors to different molecular geometries in their respective fully relaxed singlet and triplet states. Another analog DM-Me-B (Φ\textsubscript{PL:} 73% in 30 wt% in DPEPO; ΔE\textsubscript{ST:} 0.25 eV) was also developed by replacing the phenyl group onto the donor unit of DM-B with a methyl group. In contrast to DM-B (Φ\textsubscript{PL:} 96%), the slight structural change contributes to a reduction of the Φ\textsubscript{PL to 73% although DM-Me-B still maintains similar TADF properties. OLEDs based on DM-B (50 wt% in DPEPO) achieved an EQEmax of 27.4%, with only minor efficiency roll-off at a luminance of 1,000 cd m\textsuperscript{−2} where the EQE\textsubscript{1000} is 24.4%. The EQEmax of the devices based on DM-Bm (30 wt% in DPEPO) and DM-G (20 wt% in DPEPO) are 21.7% and 18.5%, respectively, which are

![Figure 33. Molecular structures and properties of TADF emitters based on TSCT mechanism.]
proportional to the $\Phi_{PL}$ of these emitters. In contrast, the devices based on the more flexible and less electronically coupled DM-X (20 wt% in DPEPO) and DM-Z (30 wt% in DPEPO) exhibit considerably lower maximum efficiencies of 4.3% and 3.2%, respectively.

Kaji et al.\cite{69} reported a TSCT compound TpAT-tFFO (Figure 35) based on the design strategy of controlling the distance and relative orientation between the adjacent tilted donor and acceptor moieties attached via the triptycene (Tp) scaffold. According to the DFT calculations, there is an increase in the energy levels of 1CT and 3CT states with increasing distance between the donor and acceptor (Figure 36b top). By contrast, the 3LE state only shows a weak dependence on the donor–acceptor distance. RISC is mediated by the intervening 3LE state between the 1CT and 3CT states, and the high $k_{RISC}$ of $1.2 \times 10^7 \text{s}^{-1}$ is ensured by the energy level matching of the three states. Importantly, the authors showed by DFT calculations that tilted face-to-face orientation between the donor and acceptor greatly enhances the SOC between the $^3$CT and $^3$LE states, which is not the case for the coplanar conformation. TpAT-tFFO exhibited strong sky-blue emission with a $\lambda_{PL}$ of 485 nm. The $\Phi_{PL}$ in toluene markedly increased from 1.8% to 84% after 30 min of Ar bubbling, while the $\Phi_{PL}$ of the film 25 wt% doped into the mCBP host and for the neat film were determined to be 76% and 71%, respectively. A device using an optimized doping concentration of 25 wt% showed an EQE$_{max}$ of 19.2%. A gentle efficiency roll-off was obtained with EQEs of 19.1% and 18.1% at 100 cd m$^{-2}$ and 1,000 cd m$^{-2}$, respectively; moreover, EQE of 14.4% and 11.6% were retained even at high luminance of 10,000 cd m$^{-2}$ and 20,000 cd m$^{-2}$.

Monkman et al.\cite{72} developed two unsymmetric donor–donor’–acceptor (D–D’–A) type emitters, Ph$_3$TRZCzTPA and Ph$_2$TRZCzTPA (Figure 35), where the co-facial overlap between D and A is controlled by the introduction of a weak (rigid) carbazole donor bridge (D’). According to the crystallographic data, the pendant (spacer) aryl rings are highly twisted from
the carbazole bridge (D') due to congested steric interactions. The short distances between the donor and acceptor enable the through space interaction. By comparing with the emission at 492 nm from the exciplex between TPA and TRZ in toluene, the identical emission observed from Ph3TRZCzTPA and Ph2TRZCzTPA indicates that the CT emission in both comes from a through-space intramolecular TRZ-TPA CT excited state. No contribution from a through-bond, TRZ—weak D' CT pair was observed. Both Ph3TRZCzTPA and Ph2TRZCzTPA have the same small ΔE_ST of 20 meV in Zeonex matrix. However, Ph2TRZCzTPA has a faster k_RISC than Ph3TRZCzTPA, which is ascribed to the more optimal tilted co-facial orientation of D and A forming the through-space CT state, which the authors contend is critical in controlling SOC and thus the RISC rate, as proposed by Kaji et al.[69] The EQE_max values of the devices based on Ph3TRZCzTPA (20 wt% in 26DCzPPy) and Ph2TRZCzTPA (12 wt% in CBP) are 13.3% and 16.3%, respectively, which correlate with the relative RISC rates of the materials.

The π-stacked scaffold has also been expanded to spatially confine donor/acceptor/donor (D/A/D) motifs.[73] Similar to the monomer analogs of DM-B and DM-Bm,[70] DM-BD1 and DM-BD2 also rely on spatially confined donor—acceptor interaction but with two donors within one molecule in a sandwich-like structure (Figure 35). The single-crystal structures of DM-BD1 and DM-BD2 are shown in Figure 37. The additional donor is asserted to be helpful in realizing a more parallel D/A alignment, which results in a small ΔE_ST (0.00 eV for DM-BD1 and —0.07 eV for DM-BD2) and fast k_RISC (2.9 × 10^5 s⁻¹ for DM-BD1 and 3.1 × 10^5 s⁻¹ for DM-BD2). The torsion angles between the donor and acceptor moieties were determined to be 30° for DM-BD1 and 25° for DM-BD2 from the crystal structures, where the not quite co-facial orientation has been demonstrated by Kaji et al.[69] to be critical to turn on spin–orbit coupling and facilitate RISC. Interestingly, both compounds showed broad, structure-less CT emission that are almost identical to those in solution, with a λ_PL of 495 nm. The Φ_PL of DM-BD1 (10 wt% doped in DPEPO matrix) and DM-BD2 (10 wt% doped in DPEPO matrix)
were determined to be 94.2% and 92.8%, respectively. The near unity $\Phi_{PL}$ provides evidence of the effectiveness of this strategy to suppress nonradiative loss mechanisms. The best OLEDs contained a 30 wt% emitter and showed EQE$_{\text{max}}$ of 28.0% and 26.6%, respectively, for devices with DM-BD1 and DM-BD2, corresponding to CIE coordinates of (0.21, 0.47) and (0.20, 0.46), respectively.

To enhance the D–A electronic interactions by adjusting the D–A distance, Zhang et al.\[74\] employed a xanthene bridge in two TSCT TADF emitters, mCz-Xo-TRZ and dCz-Xo-TRZ.

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**Figure 36.** a) Structures of the donor (blue) and acceptor (red) segments (top). The donor and acceptor have a tilted ($\approx$10°) face-to-face alignment and are spatially separated at a certain distance, $d_{DA}$. HOMO and LUMO with $d_{DA}$ of 4.72 Å (bottom). b) DFT-calculated energy levels of $S_1$, $T_1$, $^3$LE$_D$, and $^3$LE$_A$ (top), $\Delta E_{\text{CT}}$ (middle) and $f$ (bottom) as a function of $d_{DA}$, where $^3$LE$_D$ and $^3$LE$_A$ denote the $^3$LE states on the donor and acceptor segments, respectively. The vertical green dashed line indicates $d_{DA} = 4.72$ Å, which corresponds to $d_{DA}$ of a DFT-optimized structure for TpAT-tFFO at the ground state. The blue, red, and green shaded regions highlight the energy levels of the $^3$LE$_D$, $^3$LE$_A$, and $^3$CT states, respectively. Reproduced with permission.[69] Copyright 2020, Nature Portfolio.

**Figure 37.** Single-crystal structures (hydrogen atoms are omitted) of DM-BD1 (left) and DM-BD2 (right). Reproduced with permission.[73] Copyright 2021, Wiley-VCH.
that possess space-confined face-to-face D–A alignment and minimized D–A distance down to 2.7–2.8 Å, which is shorter than twice the van der Waals radius of a carbon atom (1.7 Å). As a result, the greatly strengthened electronic interaction between D and A leads to fast $k_r$ of 9.9 and 8.7 $/C^2_0$ 106 s$^{-1}$ for mCz-Xo-TRZ and dCz-Xo-TRZ, respectively. The stronger donor in dCz-Xo-TRZ versus mCz-Xo-TRZ leads to a red-shift of the PL spectrum in toluene (from 454 to 461 nm) and the 30 wt% doped film in bis(diphenylphosphinyl)-dibenzofuran (PPF) matrix (from 469 to 482 nm). The $\Phi_{PL}$ values of 90% and 92% for mCz-Xo-TRZ and dCz-Xo-TRZ, respectively, are high; however, the $k_{RISC}$ values are 3.0 $/C^3_{0}10^5$ s$^{-1}$ and 3.3 $/C^3_{0}10^5$ s$^{-1}$, respectively, which are significantly slower than that of TpAT-tFFO (1.2 $/C^3_{0}10^7$ s$^{-1}$). The blue OLEDs showed broad emission with $\lambda_{EL}$ of 477 and 464 nm for devices with dCz-Xo-TRZ and mCz-Xo-TRZ, corresponding to the CIE coordinates of (0.16, 0.29) and (0.15, 0.20), respectively. The EQEmax of 27.8% for the device with dCz-Xo-TRZ and 21.0% for the device with mCz-Xo-TRZ showed only modest efficiency roll-off where the EQE values remained at 24.0% and 17.1% at a luminance of 1000 cd m$^{-2}$.

Zysman-Colman and co-workers recently reported a systematic study that documented explicitly in the PL spectrum emission from a TSCT in the compound TPA-ace-TRZ$^{[75]}$ (Figure 39). This work provides a direct evidence that the TSCT plays a major role in the communication between the donor and acceptor. The photophysical studies in toluene of TPA-ace-TRZ show two characteristic lifetimes corresponding to the fast-decaying through-bond CT (TBCT) state ($\tau_{PL} = 9.6$ ns) and longer lived TSCT state ($\tau_{PL} = 51$ ns). The existence of the two different CT states was ascribed to rapid decay from the initially populated TBCT state (with moderate D–A dihedral angles of 48° between the TPA and ace units and 57° between the ace and TRZ units) to the more stable TSCT state. The $\Phi_{PL}$ of TPA-ace-TRZ was measured to be only 17%, which is due to the weak electronic communication between the donor and acceptor through the ace bridge (the ace unit is orthogonal and electronically decoupled from both D and A groups). It was found the the lowest-energy triplet state resides on the ace bridge, which also leads to a large $\Delta E_{ST}$ of 0.48 eV (determined in 1 wt% ZEONEX film). The weak electronic communication makes it difficult for the triplet harvesting through the spin-vibronic coupling mechanism because the potentially mediating local triplet state resides on the ace bridge, which is orthogonal to both D and A and thus cannot efficiently couple to the TSCT state. Therefore, even though TPA-ace-TRZ possesses a strong TSCT state, it can hardly produce TADF because of the lack of coupling to a mediating LE triplet state. This study reveals the intimate interplay that the bridging ace group has on mediating both the TBCT state and the TSCT state.

Wang et al.$^{[76]}$ incorporated TSCT states in the design of two star-shaped TADF emitters, containing DMAC (Ac3TRZ3) or a dendritic teracridan (TAc3TRZ3) as donors and TRZ as acceptors about a hexaphenylbenzene scaffold (Figure 40). Because of the...
steric hindrance inherent in the structure both molecules adopt a propeller-shaped conformation in which the peripheral aromatic units are almost perpendicular to the central phenyl ring. As a result of the strong TSCT character coupled with the weak TBCT character due to the physical separation of donors and acceptors, both molecules show small $\Delta E_{ST}$ values of 0.04 eV for TAc3TRZ3 and $-0.08$ eV for Ac3TRZ3. The negative $\Delta E_{ST}$ is likely due to different molecular geometries in the fully relaxed singlet and triplet states as also identified in DM-Bm and DM-G. Compared to Ac3TRZ3 ($\Phi_{PL}$: 54% 10 wt% in Ac6 (control compound contains six acridan donors), TAc3TRZ3, containing the stronger dendritic donor, shows a higher $\Phi_{PL}$ of 63% (10 wt% in Ac6). The authors ascribed this higher photoluminescence quantum yield to the more efficient charge transfer in TAc3TRZ3 mediated by the spatial $\pi-\pi$ interactions. The use of the stronger dendritic donors also leads to a red-shift of the emission spectrum from $\lambda_{PL}$ of 486 nm for Ac3TRZ3 to $\lambda_{PL}$ of 508 nm for TAc3TRZ3. The nondoped OLEDs showed EQE$_{max}$ of 3.5% and 3.1% for the devices with Ac3TRZ3 [$\lambda_{EL}$: 492 nm; CIE = (0.22, 0.42)] and TAc3TRZ3 [$\lambda_{EL}$: 503 nm; CIE = (0.25, 0.47)], respectively. However, the doped devices showed improved EQE$_{max}$ of 11.0% and 14.2% for the devices with Ac3TRZ3 [$\lambda_{EL}$: 520 nm; CIE = (0.30, 0.54)] and TAc3TRZ3 [$\lambda_{EL}$: 538 nm; CIE = (0.22, 0.48)], respectively.

Wang et al. [77] also prepared a series of blue TADF polymers that exploit only TSCT to electronically couple donor and acceptor moieties (Figure 41). The polymers use a nonconjugated polyethylene backbone, 9,9-dimethyl-10-phenyl-acridan (Ac) or 9,9-bis(1,3-di-tert-butylphenyl)-10-phenyl-acridan (TBAc) as the donor pendant and TRZ as the acceptor pendant. In this design, D and A units are not directly electronically decoupled, but are spatially close to each other, allowing through-space, rather than the TBCT processes to occur. The TSCT character observed from the Ac-based polymer results in both a small $\Delta E_{ST}$ of 0.019 eV and moderate $\Phi_{PL}$ of 60% in the neat film. In comparison, the TBAc-based polymers only exhibited fast prompt fluorescence emission without TSCT contribution because the sterically hindered 1,3-dibutylphenyl groups separate the electron-donating acridan unit from the electron-accepting triazine unit, which weakens the TSCT transition. The device with a polymer consisting of 95 mol% Ac and 5 mol% TRZ content demonstrated the best device performance with CIE coordinates of (0.18, 0.27) and an EQE$_{max}$ of 12.1%. The optoelectronic properties of the aforementioned materials are summarized in Table 15, and the device performance metrics are summarized in Table 16.

10. Chiral TADF Emitters Containing Triazine

Circularly polarized luminescence (CPL) materials have attracted great attention due to their potential applications in optical data storage,[78] chirality sensing,[79] organic electronic devices,[80] and bio imaging.[81] In 1997, Meijer et al. [82] developed the first example of a circularly polarized OLED (CP-OLED). Since then, many chiral emitters have been explored, including chiral polymers,[83]...
chiral phosphorescent complexes \cite{84} and chiral TADF small molecules \cite{85}. Of the latter, there are a few examples of chiral TADF emitters incorporating a triazine acceptor.

In 2019, Zysman–Colman and co-workers \cite{15} introduced the carbazolophane (Czp) donor unit (indolo[2,2]paracyclophane) for the design of chiral TADF emitters, R_{S}-CzpPhTrz and S_{S}-CzpPhTrz (Figure 42). The bulky carbazolophane donor unit increased the torsion between the donor and the phenylene bridge compared to the control compound CzPhTrz (same structure as CzTRZ discussed in Section 2). As discussed above, CzPhTrz was known to be a non-TADF compound; however, the larger torsion between the donor and the bridge in CzTRZ leads to a decreased $\Delta E_{ST}$ of 0.16 eV, which contributes to the turn on of the TADF. rac-CzpPhTrz is a sky-blue emitter with $\lambda_{PL}$ of 482 nm, and high $\phi_{PL}$ of 69% in 10 wt% doped DPEPO films. The chiroptical properties of the enantiomers R_{P}-CzpPhTrz and S_{P}-CzpPhTrz reveal mirror image circular dichroism (CD) and CPL, with $g_{sum}$ values of $5 \times 10^{-3} - 7 \times 10^{-4}$, respectively. Sky blue-emitting OLEDs were fabricated with an EQE$_{max}$ of 17% and associated CIE coordinates of (0.17, 0.25).

Zheng et al. \cite{86} reported a pair of chiral TADF emitters (Figure 42), R_{S}5 and S_{S}5, by combining a TRZ acceptor with a chiral donor group (PXZp). PXZp is a phenoxazine derivative containing an annulated [2,2]paracyclophane (pCp) skeleton which has ever been demonstrated as an efficient unit enabling a blue chiral TADF emitters by Zysman–Colman and co-workers in 2019. \cite{15} Similar to their analog PXZ-TRZ (R_{P}5: 540 nm; $\phi_{PL}$: 66%; $\tau_{PL}$: 1.1 $\mu$s in 8 wt% mCPCN; $\Delta E_{ST}$: 0.017 eV), R_{S}5 and S_{S}5 exhibited broad PL with $\lambda_{PL}$ of 548 nm (in toluene), 539 nm (in neat film), and 527 nm (in 10 wt% CBP film). A moderate $\phi_{PL}$ of 60% as well as a small $\Delta E_{ST}$ of 0.03 (in 10 wt% CBP film) resemble the photophysical properties of PXZ-TRZ, indicating the weak influence from the pCp on the TADF properties. The dissymmetry values, $g_{sum}$, of R_{S}5 and S_{S}5 (Figure 43) are $-2.4 \times 10^{-3} + 3.3 \times 10^{-3}$ and $-2.3 \times 10^{-3} + 2.7 \times 10^{-3}$ in toluene ($1 \times 10^{-5}$ mol L$^{-1}$) and neat films, respectively, which are typical values from organic emitters. Solution-processed CP-OLEDs showed EQE$_{max}$ of 7.8%/7.1% and $g_{EL}$ of $+1.4 \times 10^{-3}/-2.0 \times 10^{-3}$. Although the nondoped devices based on S_{S}5/R_{S}5 possessed lower EQE$_{max}$ of 2.3%/1.8%, however, the $g_{EL}$ improved modestly to $+4.3 \times 10^{-3}/-4.6 \times 10^{-3}$.

A pair of triptycene-based enantiomers, (S,S)/(R,R)-TpAc-TRZ \cite{87} were developed containing a triptycene-fused diacridine chiral donor (S,S)/(R,R)-TPAc (Figure 42). The compounds can be recognized as the combination of two well-known DMAC-TRZ TADF emitters through a nonconjugate 3D triptycene bridge. Therefore, the excellent TADF properties of DMAC-TRZ are still maintained for the enantiomers, especially the suppression of concentration quenching in these neat films. The (S,S)-TpAc-TRZ neat film ($\lambda_{PL}$: 541 nm; $\phi_{PL}$: 85%; $\tau_{PL}$: 1.1 $\mu$s; $\Delta E_{ST}$: 0.03 eV) showed photophysical properties reminiscent to those of the DMAC-TRZ in neat film ($\lambda_{PL}$: 500 nm; $\phi_{PL}$: 83%; $\tau_{PL}$: 3.6 $\mu$s; $\Delta E_{ST}$: 0.05 eV), except for the 41 nm red-shift in the PL. The circular dichroism (CD) spectra of (S,S)-(+)TpAc-TRZ and (R,R)-(−)-TpAcTRZ exhibited clear mirror-image relationship with alternating positive and negative cotton effects (Figure 44). The $g_{CD}$ values are $+1.9 \times 10^{-3}$ for (S,S)-(+)TpAc-TRZ and $-1.8 \times 10^{-3}$ for (R,R)-(−)-TpAc-TRZ in neat films. Due to the high molecular weight of the emitters, only solution-processed OLEDs were fabricated, with an EQE$_{max}$ of 25.5% ($\lambda_{EL}$ 534 nm). However, a significant efficiency roll-off was observed and the EQE decreased to 1.6% at a luminance of 1000 cd m$^{-2}$. 


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**Figure 41.** Molecular structures and properties of TADF polymer emitters with nonconjugated backbone and TSCT effect.
Similar to $g_{PL}$, the $g_{EL}$ values reached to $+1.5 \times 10^{-3}$ for the ($S,S$)-$\ell$-TpaCT-TRZ-based device and $-2.0 \times 10^{-3}$ for ($R,R$)-$\ell$-TpaCT-TRZ-based device.

Chen et al. reported a pair of macrocyclic TADF emitters ($\ell$)-($R,R$)-MC and ($\ell$)-(S,S)-MC linking chiral octahydroquinaphthyl units with a DMAC-TRZ derivative (Figure 42). The four-unit nonconjugated macrocycle consisting of two donors and two acceptors shows TADF. Similar to DM-TRZ, the enantiomers ($\ell$)-(R,R)-MC and ($\ell$)-(S,S)-MC showed a small $\Delta E_{ST}$ of 0.067 eV, a short $\tau_d$ of 1.5 μs, suppressed concentration quenching in neat films and $\Phi_{PL}$ of 79.7% (25 wt% ($\ell$)-(R,R)-MC: CBP). The $g_{PL}$ of 2.2 $\times 10^{-3}$ in solution (Figure 45) and mirror image CD spectra are typical for chiral TADF emitters. The solution-processed CP-OLEDs (25 wt% ($\ell$)-(R,R)-MC/ ($\ell$)-(S,S)-MC: CBP) displayed EQEmax of 17.1%/15.5% and $g_{EL}$ of 1.5 $\times 10^{-3}$/1.7 $\times 10^{-3}$.

Based on the molecule structure of DM-B, Jiang et al. reported two chiral derivatives SFST and SFOT (Figure 46), which contain asymmetric donors with either PTZ or PXZ attached onto the spiro-skeleton linkage. Similar to DM-B, both SFST ($\lambda_{PL}$: 512 nm; $\Phi_{PL}$: 53.1%; $\tau_d$: 6.78 μs; $\Delta E_{ST}$: 0.052 eV; 30 wt% in mCBP) and SFOT ($\lambda_{PL}$: 512 nm; $\Phi_{PL}$: 89.0%; $\tau_d$: 7.98 μs; $\Delta E_{ST}$: 0.053 eV; 30 wt% in mCBP) are TSCT emitters where the donor and acceptor are aligned in a near co-facial manner. The difference between SFST and SFOT is based on the heteroatoms contained within the donor. As shown in Figure 47, the CD spectra of ($R$)-SFST/($S$)-SFST and ($R$)-SFOT/($S$)-SFOT show the typical mirror-image feature of enantiomeric molecules. The dissymmetry values $g_{lum}$ of ($S$)-SFOT/($R$)-SFOT in toluene are 2.2 $\times 10^{-3}$ and $-2.0 \times 10^{-3}$, respectively. Interestingly, the $g_{lum}$ values of ($S$)-SFOT/($R$)-SFOT are almost twice those of ($S$)-SFOT/($R$)-SFOT, at 3.4 $\times 10^{-3}$ and $-4.0 \times 10^{-3}$, respectively. This change can be attributed to the more distorted structure of SFST due to the presence of the larger sulfur atom. The CPEL signals of the CP-OLEDs, $g_{EL}$, are 1.30 $\times 10^{-3}$ and 1.0 $\times 10^{-3}$ for the devices with ($S$)-SFST and ($S$)-SFOT, respectively.

Based on the same design strategy and structurally similar to SFST and SFOT, another analog SDMAC (Figure 48) has also been reported by Jiang et al. SDMAC also shows CPL emission, as well as aggregation-induced emission enhancement (AIEE), solvatochromic, and piezochromic luminescence. It is reasonable to speculate that the analogs SFST and SFOT can also possess these same multistimulus response properties because

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Table 15. Summary of photophysical and electrochemical properties.

| Emitter | Solution $\lambda_{PL}/\Phi_{PL}/\tau_d$ (medium) | Solid State $\lambda_{PL}/\Phi_{PL}/\tau_d$ (medium) | $\Delta E_{ST}$ | HOMO | LUMO | Ref. |
|---------|-----------------------------------------------|-----------------------------------------------|----------------|-------|-------|------|
| XPT     | 562/7.7/2.3 (PhMe)                            | $-$ /66 /($-$ (10 wt% in DPEPO) | $-$ | $-$ | $-$ | [63] |
| XCT     | 419/5.9/3.0 (PhMe)                            | $-$ /$-$ /$-$ | $-$ | $-$ | $-$ | [63] |
| XibCT   | 451/6/2.0 (PhMe)                             | $-$ /35 /($-$ (10 wt% in DPEPO) | $-$ | $-$ | $-$ | [63] |
| oBFCT   | 480/10/3.7 (PhMe)                            | $-$ /$-$ /$-$ | 0.002 | $-$ | $-$ | [64] |
| mBFCT   | 450/10/3.7 (PhMe)                            | $-$ /31.1/2.9 (in neat film) | 0.19 | $-$ | $-$ | [64] |
| pBFCT   | 430/10/3.7 (PhMe)                            | $-$ /85.3/31.2 (in neat film) | 0.30 | $-$ | $-$ | [64] |
| oBFCT   | $-$ /$-$ /$-$ | $-$ /100 /($-$ (8 wt% in DPEPO) | $-$ | $-$ | $-$ | [65] |

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of their similar molecule framework. SDMAC has a smaller $\Delta E_{CT}$ of 0.034 eV than that of SFST and SFOT, which is evidenced by the shortest delayed emission lifetime of 4.17 μs in contrast to 6.78 μs and 7.98 μs for SFST and SFOT, respectively. The $\Phi_{PL}$ is 90% in a doped film containing 30 wt% SDMAC in 2,8-bis (diphenylphosphoryl)dibenzo[b,d]furan (PPF). Both the CD and

### Table 16. Summary of device structures and performances.

| Emitter     | Device Structure                          | $E_{L_{\text{max}}}$ [nm] | CIE   | $V_{on}$ [V] | EQE/PE/CE<sup>a</sup> | EQE<sub>100/1000 [cd] m</sub><sup>-2</sup> | Ref. |
|-------------|------------------------------------------|--------------------------|-------|-------------|------------------------|---------------------------------|------|
| XPT         | ITO/TAPC/DPEPO: 10% emitter/DPEPO/TmPyPb/LiF/Al | 584          | –     | ≈3.2       | 10/–/–                | –/–                            | [63] |
| XIbCT       | ITO/TAPC/DPEPO: 10% emitter/DPEPO/TmPyPb/LiF/Al | 488          | –     | ≈4.0       | 4/–/–                 | –/–                            | [63] |
| oBF<sub>CzTRZ</sub> | ITO/PEDOT-PSS/TACP/mCP/DPEPO:20% oBF<sub>CzTRZ</sub>/TSPO1/TPB/LiF/Al | 477 (0.18, 0.31) | –     | 20.4/–/– | 20.0/17.4             | –/–                            | [64] |
| mBF<sub>CzTRZ</sub> | ITO/PEDOT-PSS/TACP/mCP/DPEPO:20% mBF<sub>CzTRZ</sub>/TSPO1/TPB/LiF/Al | 473 (0.17, 0.25) | –     | 13.2/–/– | ≈8.0/≈2.0             | –/–                            | [64] |
| pBF<sub>CzTRZ</sub> | ITO/PEDOT-PSS/TACP/mCP/DPEPO:20% pBF<sub>CzTRZ</sub>/TSPO1/TPB/LiF/Al | 465 (0.15,0.18) | –     | 16.7/–/– | ≈10.0/≈5.0             | –/–                            | [64] |
| DPA–o–TRZ  | ITO/PEDOT-PSS/TACP/mCP/TSPO1: 5% emitter/TSPO1/LiF/Al | 497 (0.21, 0.45) | ≈4.2 | 17.2/34.5/45 | ≈16.0/10.5             | –/–                            | [65] |
| MPA–o–TRZ  | ITO/PEDOT-PSS/TACP/mCP/TSPO1: 5% emitter/TSPO1/LiF/Al | 532 (0.35, 0.58) | ≈4.2 | 16.3/41.9/54.7 | ≈15.0/12.7             | –/–                            | [65] |
| BC<sub>2</sub>TZ<sub>D</sub>BF | ITO/DNTPD/BBPBA/PcAc/mCBP/TSQZ.5 wt% BC<sub>2</sub>TZ<sub>D</sub>BF/DEBT/TSQZ/ZN/NS/LiF/Al | –/≈490 (0.24, 0.52) | –     | 20.1/35.1/59.6 | ≈20.0/≈15.0             | –/–                            | [67] |
| TC<sub>2</sub>TZ<sub>D</sub>BF | ITO/DNTPD/BBPBA/PcAc/mCBP/TSQZ.5 wt% TC<sub>2</sub>TZ<sub>D</sub>BF/DEBT/TSQZ/ZN/NS/LiF/Al | –/≈500 (0.27, 0.57) | –     | 23.5/44.7/74.8 | ≈23.0/≈20.0             | –/–                            | [67] |
| IDC<sub>2</sub>TZ<sub>D</sub>BF | ITO/DNTPD/BBPBA/PcAc/mCBP/TSQZ.5 wt% IDC<sub>2</sub>TZ<sub>D</sub>BF/DEBT/TSQZ/ZN/NS/LiF/Al | –/≈485 (0.22, 0.48) | –     | 12.2/19.3/33.6 | ≈12.0/≈11.0             | –/–                            | [67] |
| SF120Tz     | ITO/MoO3/TAPC/mCP/DPEPO: 20% SF120Tz/DPEPO/TmPyPb/LiF/Al | 496 (0.23, 0.47) | 2.9   | 22.4/59.1/60.4 | 22.3/20.0             | –/–                            | [68] |
| SF230Tz     | ITO/MoO3/TAPC/mCP/DPEPO: 20% SF230Tz/DPEPO/TmPyPb/LiF/Al | 484 (0.19, 0.35) | 3.2   | 19.6/45.5/46.9 | 18.9/15.9             | –/–                            | [68] |
| SF340Tz     | ITO/MoO3/TAPC/mCP/DPEPO: 20% SF340Tz/DPEPO/TmPyPb/LiF/Al | 482 (0.18, 0.37) | 3.2   | 14.6/31/31.4  | 8.5/3.1               | –/–                            | [68] |
| DM–Me–B     | ITO/HAT–CN/TACP/TCTA/mCP/DPEPO:30% emitters/DPEPO/TmPyPb/Liq/Al | 500 (0.26, 0.48) | –     | 19.2/–/–     | ≈19.0/16.8             | –/–                            | [71] |
| DM–B        | ITO/HAT–CN/TACP/TCTA/mCP/DPEPO:50% emitters/DPEPO/TmPyPb/Liq/Al | ≈488 (0.20, 0.44) | 2.8   | 27.4/68.1/–   | ≈27.0/24.4             | –/–                            | [70] |
| DM–Brn      | ITO/HAT–CN/TACP/TCTA/mCP/DPEPO:30% emitters/DPEPO/TmPyPb/Liq/Al | ≈500 (0.22, 0.48) | 2.6   | 21.7/62.7/–   | ≈21.0/19.7             | –/–                            | [70] |
| DM–G        | ITO/HAT–CN/TACP/TCTA/mCP/DPEPO:20% emitters/DPEPO/TmPyPb/Liq/Al | ≈500 (0.24, 0.50) | 3     | 18.5/47.5/50  | ≈18.0/15.4             | –/–                            | [70] |
| DM–X        | ITO/HAT–CN/TACP/TCTA/mCP/DPEPO:20% emitters/DPEPO/TmPyPb/Liq/Al | ≈500 (0.23, 0.45) | 3.4   | 4.3/10/–/–    | –/–                            | [70] |
| DM–Z        | ITO/HAT–CN/TACP/TCTA/mCP/DPEPO:30% emitters/DPEPO/TmPyPb/Liq/Al | ≈488 (0.19, 0.35) | 3.9   | 3.2/5.1/–/–   | –/–                            | [70] |
| Ac<sub>3</sub>TZ3 | ITO/PEDOT-PSS/Ac6: 10 wt% Ac3TRZ3/TSPO1/TmPyPb/LiF/Al | 492 (0.22, 0.42) | 2.9   | 11/–/30.3    | 10.4/6.6               | –/–                            | [76] |
| TA<sub>3</sub>TZ3 | ITO/PEDOT-PSS/ Ac6: 10 wt% TA3TRZ3/TSPO1/TmPyPb/LiF/Al | 503 (0.25, 0.47) | 2.9   | 14.2/–/40.6  | 13.5/10.4              | –/–                            | [76] |
| P–Ac<sub>5</sub>–TRZ50 | ITO/PEDOT-PSS: EML/TSPO1/TmPyPb/LiF/Al | 497 0.222, 0.428 | 3.4   | 3.1/–/8.5    | 3.0/3.0                | –/–                            | [77] |
| P–Ac<sub>95</sub>–TRZ50 | ITO/PEDOT-PSS/polymer/TSPO1/TmPyPb/LiF/Al | 472 0.176, 0.269 | 3.2   | 12.1/–/24.8  | 12.0/11.5              | –/–                            | [77] |
| P–T<sub>B</sub>Ac<sub>50</sub>–TRZ50 | ITO/PEDOT-PSS/polymer/TSPO1/TmPyPb/LiF/Al | 453 0.235, 0.243 | 3.8   | 0.21/–/0.6   | 0.18/–                 | –/–                            | [77] |
| P–T<sub>B</sub>Ac<sub>95</sub>–TRZ50 | ITO/PEDOT-PSS/polymer/TSPO1/TmPyPb/LiF/Al | 445 0.207, 0.196 | 5.8   | 0.33/–/0.51  | 0.14/–                 | –/–                            | [77] |
CPL spectra of the enantiomers (R)-SDMAC and (S)-SDMAC measured in dilute dichloromethane solutions (10 \textsuperscript{-5} M) exhibit mirror symmetry. The g\textsubscript{sum} values of (R)-SDMAC and (S)-SDMAC are \(-1.19 \times 10^{-3}\) and \(+1.39 \times 10^{-3}\), respectively, while the CP-OLEDs showed relatively lower g\textsubscript{EL} values than g\textsubscript{sum} of \(-8.43 \times 10^{-4}\) and \(+9.80 \times 10^{-4}\) for (R)-SDMAC and (S)-SDMAC, respectively. The OLED device (30 wt\% of SDMAC doped into PPF) was also optimized by adjusting the thickness of the electron injection layer (TmPyPB) from 25 nm to 40 nm. An EQEmax of 28.4\% was achieved at 35 nm thickness of the EIL, and it remained as high as 24.5\% at 100 cd m\textsuperscript{-2}; however, the EQE then dropped by 40\% to 17.1\% at 1000 cd m\textsuperscript{-2} (Table 17 and 18).
11. TADF Emitters Based on Triazine and Other Donors

In addition to carbazole, many alternative N-heterocycle donors have also been investigated as building blocks in triazine-based TADF emitters. 9,9-dimethyl-9,10-dihydroacridine (DMAC), 10H-phenoxazine (PXZ), and 10H-phenothiazine (PTZ) are the most popular six-membered N-heterocyclic donors used in the design of TADF emitters. The sequence of electron-donating strength typically follows PTZ > PXZ > DMAC > carbazole, with carbazole being the weakest donor. Unlike carbazole, the use of these larger N-heterocyclic donors generally produces a highly twisted conformation between the donor and the bridging units when they are N-bound because of the increased steric hindrance. As a result, the highly twisted conformation leads to a greater separation of the FMOs, which generally results in a small $\Delta E_{ST}$.

Wu et al.\cite{wu2013} reported what is now considered one of the most widely studied TADF emitters, DMAC-TRZ ($\lambda_{PL}$: 495 nm; $\Phi_{PL}$: 90%; $\tau_d$: 1.9 $\mu$s; $\Delta E_{ST}$: 0.05 eV; in 8 wt% mCPCN), as shown in Figure 49. DMAC-TRZ shows high $\Phi_{PL}$ (90%) in an 8 wt% mCPCN doped film, which is not much reduced in the neat film (83%). The EQE$_{max}$ of doped and non-doped device based on DMAC-TRZ were reported to be 26.5% and 20%, respectively, reflecting in part the differences in $\Phi_{PL}$. Due to its good solubility, a solution-processed non-doped OLED showed only a slightly lower EQE$_{max}$ of 17.6%. Hu et al.\cite{hu2020} observed that photoexciting CT states can lead to a magneto-PL signal in the SOC regime, but not found when photoexciting LE states. This is the first experimental evidence that SOC is produced in CT states. Furthermore, they found that the DMAC-TRZ-based OLEDs demonstrated magneto-EL in the high field regime (>10 mT).\cite{hu2020} This high-field magneto-EL signal provides direct evidence to indicate that the SOC is indeed enhanced, in the absence of heavy elements, towards developing spin-dependent TADF in OLEDs. Compared with DMAC-TRZ ($\lambda_{PL}$: 495 nm; $\Phi_{PL}$: 90%; $\tau_d$: 1.9 $\mu$s; $\Delta E_{ST}$: 0.05 eV; in 8 wt% mCPCN), the emission spectrum of PXZ–TRZ ($\lambda_{PL}$: 540 nm; $\Phi_{PL}$: 66%; $\tau_d$: 1.1 $\mu$s in 8 wt% mCPCN; $\Delta E_{ST}$: 0.017 eV) is red-shifted by about 45 nm due to the enhanced electron-donating ability of the PXZ. Even though both compounds show similarly small $\Delta E_{ST}$ and relatively short delayed fluorescence lifetimes ($\tau_d$: 1.1 $\mu$s; $\Delta E_{ST}$: 0.017 eV; 8 wt% PXZ–TRZ in mCPCN), the much lower $\Phi_{PL}$ of PXZ–TRZ (66% in 8 wt% mCPCN) indicates greater nonradiative decay, which

Figure 43. a) CD and b) CPL spectra of $\text{Sp-S/R}_{\text{p}}$-5. Reproduced with permission.\cite{wu2021} Copyright 2021, Wiley-VCH.

Figure 44. a) CD and CPL spectra of (S,S)/-(R,R)-TpAc-TRZ in neat film states. b) $g_{PL}$ versus wavelength curves of (S,S)/-(R,R)-TpAc-TRZ in neat film states. Reproduced with permission.\cite{hu2021} Copyright 2021, Wiley-VCH.
Figure 45. a) CD and CPL spectra and b) $g_{\text{PL}}$ versus wavelength curves of $(+)-(R,R)/(\text{S},\text{S})$-MC in toluene ($c = 1 \times 10^{-4}$ M). c) CPL spectra and d) $g_{\text{PL}}$ versus wavelength curves of $(+)-(R,R)/(\text{S},\text{S})$-MC in neat film and doped film (25 wt% macrocyclic enantiomers: CBP).

Figure 46. Representative CP-TADF molecular structures. Reproduced with permission. Copyright 2020, American Chemical Society.
may be ascribed to the energy gap law.\cite{91} An OLED containing 6 wt% PXZ–TRZ doped in CBP as the emitter layer exhibited an EQE\textsubscript{max} of 12.5% (λ\textsubscript{EL} of 529 nm).\cite{93} The authors also demonstrated that the orientation of the TDM of PXZ-TRZ can be modulated in mCBP by varying the temperature on the ITO glass holder during the deposition of the emitting layer. The horizontal orientation of the TDM of PXZ-TRZ can be enhanced by lowering the temperature of the ITO glass from 300 K to 200 K. As a result, the EQE\textsubscript{max} is improved from 9.6% at 300 K to 11.9% at 200 K.\cite{94}

The use of PTZ as a donor introduces additional conformational dynamics due to the existence of two ground-state conformers resulting from puckering of the PTZ ring, each with their own associated ΔE\textsubscript{ST}.\cite{95} PTZ-TRZ shows a slightly red shifted emission maximum (λ\textsubscript{PL}: 562 nm; in toluene) and similar Φ\textsubscript{PL} (65.8%; in 2 wt% mCBP) to those of its analog PXZ–TRZ (545 nm in toluene, Φ\textsubscript{PL} 65.7%; 6 wt% in CBP),\cite{93} while the ΔE\textsubscript{ST} (0.07 eV) of PTZ-TRZ is the largest amongst the three compounds: DMAC-TRZ, PXZ–TRZ, and PTZ-TRZ. The relatively similar electron-donating strength of the PXZ and PTZ groups in PXZ–TRZ and PTZ–TRZ translates to similar emission spectra and Φ\textsubscript{PL}. The device containing PTZ-TRZ exhibited an EQE\textsubscript{max} of 10.8%, which is also of similar performance to that of PTZ-TRZ-based OLED although the two reports\cite{93,95} used different hosts within the emissive layer. The EL spectrum shows two emission bands, one high-energy band at around 393 nm and a stronger broad band at 532 nm, resulting from the simultaneous emission from the two conformers.
3ACR-TRZ, an analog of DMAC-TRZ containing 3 donor groups, reported by Kaji et al. \[96\] shows somewhat similar photophysical properties to DMAC-TRZ, with near unity \(\Phi_{PL}\) (98%; in 16 wt% CBP) and a slightly red-shifted emission (\(\lambda_{EL}\) 504 nm; in 16 wt% CBP). The small red-shift implies that there is only a weak influence on the stabilization of the singlet state by increasing the number of DMAC units. However, the multiple donors could further delocalize the distribution of HOMO, thus leading to a smaller \(\Delta E_{ST}\) (0.015 eV). The solution-processed device showed an \(\text{EQE}_{\text{max}}\) of 18.6% at an emission of \(\lambda_{EL} \approx 520\) nm. Analog compounds containing either trisubstituted PXZ or PTZ donor groups have also been reported. \[97\] Similar evolution of the photophysical properties from the linear D-A compounds to the D\(_3\)-symmetric analogs was observed for tri-PXZ-TRZ (\(\lambda_{PL}\): 568 nm; \(\Phi_{PL}\): 58% in 6 wt% mCP; \(\tau_{PL}\): 1.10 \(\mu\)s in toluene) and TRZ3(Ph-PTZ) (\(\lambda_{PL}\): 575 nm in toluene; \(\tau_{PL}\): 7.2 \(\mu\)s in 2 wt% mCP). \[98\] The OLEDs based on TRZ3(Ph-PTZ) shows yellowish-green electroluminescence with \(\lambda_{EL} \approx 550\) nm and exhibits a much higher \(\text{EQE}_{\text{max}}\) of 17.4% than those of the devices of the tri-PXZ-TRZ-based OLEDs (\(\text{EQE}_{\text{max}}\): 13.3%; \(\lambda_{EL}\): 553 nm). The Zysman–Colman group reported yellow-emitting OLEDs based on tri-PXZ-TRZ by doping the emitter into a bespoke host 4-mCBP by thus demonstrating an improved device performance with an \(\text{EQE}_{\text{max}}\) of 19.4% and a dramatically reduced efficiency roll-off (EQE = 16.0% at a luminance of 10,000 cd m\(^{-2}\)). \[99\] i-DMAC-TRZ (\(\lambda_{PL}\): 452 nm; \(\Phi_{PL}\): 55%; \(\tau_{PL}\): 1840 \(\mu\)s; \(\Delta E_{ST}\): 0.35 eV; in 3 wt% DPEPO) is a constitutional isomer of DMAC-TRZ but where the phenylene bridge is C-bound para to the nitrogen atom of the DMAC donor (Figure 50). \[100\] Distinct from the highly twisted conformation of DMAC-TRZ, such a structural change results in a flattened conformation, leading to enhanced conjugation between the DMAC and TRZ, and hence a much larger \(\Delta E_{ST}\) (0.35 eV) than that found for DMAC-TRZ (0.06 eV). Despite the emission spectrum being blue-shifted from DMAC-TRZ (\(\lambda_{PL}\): 495 nm) to i-DMAC-TRZ (\(\lambda_{PL}\): 452 nm), the \(\Phi_{PL}\) is reduced by almost half. The device-based i-DMAC-TRZ (10 wt% in mCBP) presents a deep-blue emission with \(\lambda_{EL}\) at 450 nm and CIE coordinates of (0.15, 0.11) and an \(\text{EQE}_{\text{max}}\) of 10.9%.

**DTPSAF** (\(\lambda_{PL}\): 459 nm; \(\Phi_{PL}\): 82%; in 10 wt% mCP) is the SpiroAC analog of i-DMAC-TRZ. When compared to i-DMAC-TRZ, DTPSAF has a similar \(\lambda_{EL}\) but has a higher \(\Phi_{PL}\) due to the restricted rotational flexibility conferred by the rigid bulky SpiroAC group. Addition of methyl groups on the phenylene bridge of DTPSAF to generate DTTPSAF further enhances the restriction of the rotation and produces a more twisted
conformation, leading to a near unity $\Phi_{PL}$ and a 9 nm blue-shift in the emission for DTTSAF ($\lambda_{PL}: 450$ nm; $\Phi_{PL}: 100\%$ in 10 wt\% mCP) and DTXSAF ($\lambda_{PL}: 446$ nm; $\Phi_{PL}: 98\%$ in 10 wt\% mCP), which contain toleneyl and xylenyl bridges, respectively. Distinct to i-DMAC-TRZ, there is no reported TADF in these analogs, which based on DFT calculations can be ascribed to their too large $\Delta E_{ST}$ values. The EQEs of the DTTSAF- and DTXSAF-doped OLEDs (6.2 and 7.7\%, respectively) were higher than that of the DTPSAF-doped device (5.7\%) due to the higher $\Phi_{PL}$ values of DTTSAF ($\Phi_{PL}: 100\%$) and DTXSAF ($\Phi_{PL}: 98\%$) over that of DTPSAF ($\Phi_{PL}: 82\%$). DTXSAF-based OLEDs show the deepest blue emission with CIE coordinates of (0.15, 0.08) and $\lambda_{EL}$ of 444 nm compared to those of DTPSAF ($\lambda_{EL}$ of 460 nm) and DTTSAF ($\lambda_{EL}$ of 488 nm).  

Wu et al. reported two compounds DPAC-TRZ ($\lambda_{PL}: 478$ nm; $\Phi_{PL}: 82\%$; $\Delta E_{ST}: 0.133$ eV in 12 wt\% mCPCN) and SpiroAC-TRZ ($\lambda_{PL}: 480$ nm; $\Phi_{PL}: 100\%; \Delta E_{ST}: 0.072$ eV; in 12 wt\% mCPCN), both of which are derivatives of DMAC-TRZ but where the two methyl groups on the acridan are replaced by phenyl and 2,2′-biphenyl (spirobiphenyl), respectively. In contrast to DMAC-TRZ, the structural modifications of the donor contribute to a blue-shift of the emission. The fluorescence (phosphorescence) spectra of SpiroAC-TRZ, DPAC-TRZ, and DMAC-TRZ in 12 wt\% mCPCN films are structureless with $\lambda_{PL}$ of 480 nm (483 nm), 478 nm (482 nm), and 495 nm (504 nm), respectively. Both compounds possess small $\Delta E_{ST}$ values though larger than that of DMAC-TRZ, thus leading to relatively short delayed lifetime (DPAC-TRZ: $\tau_d$ of 2.9 $\mu$s; SpiroAC-TRZ: $\tau_d$ of 2.1 $\mu$s). DPAC-TRZ has a lower $\Phi_{PL}$ of 82\% than SpiroAC-TRZ ($\Phi_{PL}: 100\%$), the latter of which is higher compared with DMAC-TRZ ($\lambda_{PL}: 495$ nm; $\Phi_{PL}: 90\%$; $\tau_d: 1.9$ $\mu$s; $\Delta E_{ST}: 0.05$ eV; in 8 wt\% mCPCN). DPAC-TRZ and SpiroAC-TRZ have TDMs that are highly horizontally oriented, with $\theta$ of 78\% for DPAC-TRZ and 83\% for SpiroAC-TRZ, respectively. The device with SpiroAC-TRZ retains a high EQE$_{1000}$ of 30.5\% at a luminance of 1000 cd m$^{-2}$.  

Replacement of the methyl groups on the acridan with a spiro adamantyl unit, as in a-DMAC-TRZ ($\lambda_{PL}: 479$ nm; $\Phi_{PL}: 86.1\%$; $\tau_d: 4.09$ $\mu$s in 20 wt\% DPEPO; $\Delta E_{ST}: 0.20$ eV) results in a
blue-shifted emission, but with otherwise comparable photophysical properties to that of DMAC-TRZ[91] (λPL: 495 nm; ΦPL: 90%; τd: 1.9 μs; ΔE_ST: 0.05 eV; in 8 wt% mCPCN). The introduction of the rigid and bulky adamantanyl moiety not only suppresses the geometry relaxation in the excited state but also induced the formation of quasi-axial conformer (QAC) and quasi-equatorial conformer (QEC) geometries corresponding to a shoulder emission peak at around 419 nm and a main emission peak at around 479 nm in the PL spectrum, respectively. The ΔE_ST values of two conformers were confirmed separately by different excitation wavelength. With an excitation wavelength of 360 nm, the S1 and T1 energy levels of a-DMAC-TRZ were calculated to be 2.97 and 2.66 eV, demonstrating a large ΔE_ST of 0.31 eV. At an excitation wavelength of 420 nm, the S1 and T1 energy levels of a-DMAC-TRZ were calculated to be 2.79 and 2.59 eV, thus translating to a smaller ΔE_ST of

Figure 50. Molecular structures and properties of TADF emitters based on triazine and DMAC derivatives donors.

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0.20 eV. Owing to the effect of the rigid molecular backbone and the degenerate alignment of \(^1\)LE of QAC and \(^3\)CT of QEC for efficient dual fluorescence emission, the resulting OLEDs achieved a high EQEmax of 28.9% at CIE coordinates of \((0.18, 0.35)\). \(^{[104]}\)

Kaji et al.\(^{[105]}\) demonstrated that by replacing the distal phenyl groups attached to the triazine with adamantyl substituents, the acceptor becomes weaker, leading to a blue-shifted emission compared to DMAC-TRZ,\(^{[91]}\) DPAC-TRZ,\(^{[102]}\) and SpiroAC-TRZ.\(^{[102]}\) Solution-processed devices employing the emitters FA-TA \((\lambda_{PL}: 452 \text{ nm in toluene}; \Phi_{PL}: 76\%; \tau_{d}: 4.4 \mu\text{s in } 10 \text{ wt\% } \text{CzSi}; \Delta E_{ST}: 0.16 \text{ eV})\), MA-TA \((\lambda_{PL}: 469 \text{ nm in toluene}; \Phi_{PL}: 83\%; \tau_{d}: 18.3 \mu\text{s in } 10 \text{ wt\% } \text{CzSi}; \Delta E_{ST}: 0.14 \text{ eV})\), and PA-TA \((\lambda_{PL}: 450 \text{ nm in toluene}; \Phi_{PL}: 70\%; \tau_{d}: 69.5 \mu\text{s in } 10 \text{ wt\% } \text{CzSi}; \Delta E_{ST}: 0.17 \text{ eV})\) exhibited EQEmax of 11.2%, 22.3%, and 22.1% with CIE coordinates of \((0.15, 0.19)\), \((0.15, 0.13)\), and \((0.15, 0.10)\), respectively, as shown in Figure 50. MA-TA represents one of the most efficient blue emitters for solution-processed OLEDs reported to date. However, the much poorer performance of the devices with PA-TA and FA-TA is likely in part to the random orientation of the TDMs in the spin-coated films when compared to the highly horizontally oriented TDMs of DPAC-TRZ and SpiroAC-TRZ in evaporated 12 wt% mCP-CN, although the emitters are similar in structure. The higher energy excited states of PA-TA and FA-TA also make it difficult to find suitable host materials or blocking layers in devices, which might be the reason for this poor performance.

Replacement of the spiro-carbon in DPAC-TRZ\(^{[102]}\) with a silicon atom results in the emitter DTPPDDA\(^{[106]}\). This compound shows a 10 nm blue-shifted emission \((\lambda_{PL}: 468 \text{ nm}; \Phi_{PL}: 79\%; \tau_{d}: 5.1 \mu\text{s in } 10 \text{ wt\% } \text{mCP/TSPO1}; \Delta E_{ST}: 0.16 \text{ eV})\) than DPAC-TRZ \((\lambda_{PL}: 478 \text{ nm}; \Phi_{PL}: 82\%; \Delta E_{ST}: 0.13 \text{ eV})\), yet both compounds have comparable \(\Delta E_{ST}\). However, the larger silicon atom radius makes DTPPDDA more flexible, which adversely reduces its \(\Phi_{PL}\). A blue OLED with the CIE coordinates of \((0.15, 0.20)\) showed an EQEmax of 22.3%; the EQE reduced to 10.6% at 1000 cd m\(^{-2}\) when the emitter was doped in a mixed exciplex-co-host system of mCP/TSPO1.

The addition of a second phenylene ring within the bridge in DTPPDDA resulted in an increased spatial separation between the donor and acceptor, as well as an improved horizontal dipole ratio of the TDM. DTPPDDA \((\lambda_{PL}: 450 \text{ nm in toluene}; \Phi_{PL}: 38\%; \tau_{d}: 20 \mu\text{s in } 8 \text{ wt\% } \text{mCP/TSPO1}; \Delta E_{ST}: 0.04 \text{ eV})\) showed a TDM \(\theta\) value of 0.73 compared to that of DTPPDDA (0.66; isotropic). However, the extremely short “delayed lifetime” of 20 ns clearly indicates that DTPPDDA is not a TADF emitter. The biphenylene ring will adversely result in a lower local-excited triplet state energy than the energy of its lowest charge transfer triplet state \((^1\text{LE} < ^3\text{CT})\) because the former is sensitive to the enhanced conjugation while the latter is predominantly determined by the charge transfer strength. As a result, the upconversion of the triplet excitons become impossible due to its large barrier from the \(^1\text{LE}\) to the \(^3\text{S}_{1}\) state. Although the \(\Delta E_{ST}\) was determined to be as small as 0.04 eV, it does not align with this analysis. The triplet energy was determined according to the delayed fluorescence that, however, did not provide the delayed time for the measurement of phosphorescence. The OLED employing DTPPDDA showed an EQEmax of 4.7% and deep blue emission at CIE.

| Emitter       | Solution \(\lambda_{PL}/\Phi_{PL}/\tau_{d}\) (medium) | Solid State \(\lambda_{PL}/\Phi_{PL}/\tau_{d}\) (medium) | \(\Delta E_{ST}\) [eV] | HOMO [eV] | LUMO [eV] | Ref. |
|---------------|----------------------------------------------------|---------------------------------------------------|-------------------------|-----------|-----------|-----|
| DMAC-TRZ      | –/–/–                                             | 495/90/1.9 (12 wt% in mCP-CN)                       | 0.06                    | –5.61     | –3.12     | [91] |
| PKZ-TRZ       | –/29.5/0.676                                     | 540/66/1.1 (8 wt% in mCP-CN)                        | 0.02                    | –5.50     | –3.10     | [91] |
| PTZ-TRZ       | –/–/– (PhMe)                                     | 540/65/– (6 wt% in CBP)                             | 0.07                    | –5.50     | –3.00     | [95] |
| 3ACR-TRZ      | 51 194 (PhMe)                                    | 504/98/6.7 (16 wt% in CBP)                          | 0.02                    | –         | –         | [96] |
| tri-PKZ-TRZ   | 568/–/1.101 (PhMe)                               | –/58/– (6 wt% in mCP)                              | –                       | –5.70     | –3.40     | [97] |
| TRZ(Ph-PZT)   | 575/–/– (PhMe)                                   | 520/–/7.2 (2 wt% in mCP)                            | –                       | –         | –         | [104a] |
| i–DMAC-TRZ    | 432/53.4 (PhMe)                                  | 452/55/1840 (3 wt% in DPEPO)                        | 0.35                    | –         | –         | [100] |
| DPAC-TRZ      | –/–/–                                            | 478/82/2.9 (12 wt% in mCP-CN)                       | 0.13                    | –5.72     | –3.12     | [102] |
| SpiroAC-TRZ   | –/–/–                                            | 480/100/2.1 (12 wt% in mCP-CN)                      | 0.07                    | –5.70     | –3.12     | [102] |
| SpiroAC-TRZ   | –/–/–                                            | 483/98/3.9 (10 wt% in mCP/TSPO1)                    | 0.07                    | –         | –         | [102] |
| DTPPDDA       | –/–/–                                            | 468/70/5.1 (10 wt% in mCP/TSPO1)                    | 0.16                    | –         | –         | [106] |
| DTPPDDA       | –/–/– (PhMe)                                     | –/–/–                                             | –5.57                   | –2.80     | –         | [106] |
| TP–DMAC-TRZ   | –/–/– (PhMe)                                     | –/38/20 ns (8 wt% in mCP/TSPO1)                     | –                      | –6.08     | –2.83     | [107] |
| DTPSDF        | –/–/– (PhMe)                                     | 459/82/– (10 wt% in mCP-CN)                         | –5.51                   | –2.63     | –         | [101] |
| DTTSAF        | –/–/– (PhMe)                                     | 450/100/– (10 wt% in mCP-CN)                        | –5.55                   | –2.55     | –         | [101] |
| DTXSAF        | –/–/– (PhMe)                                     | 453/98/– (10 wt% in mCP-CN)                         | –5.52                   | –2.48     | –         | [105] |
| MA–TA         | 469/–/– (PhMe)                                   | –/83/18.3 (10 wt% in CzSi)                         | 0.14                    | –5.86     | –2.96     | [105] |
| FA–TA         | 452/–/– (PhMe)                                   | –/76/44.4 (10 wt% in CzSi)                         | 0.16                    | –5.91     | –2.96     | [105] |
| PA–TA         | 451/–/– (PhMe)                                   | –/70/69.5 (10 wt% in CzSi)                         | 0.17                    | –6.00     | –2.99     | [105] |
coordinates of (0.15, 0.09).\[107\] The optoelectronic characterization of the aforementioned materials is summarized in Table 19, and device performance metrics are summarized in Table 20.

### 12. Conclusions

The objective of this review is to provide a detailed overview of triazine-based TADF materials, to compare and contrast their optoelectronic properties and to report their performance as emitters in OLEDs. The emission properties of these TADF emitters were mainly modulated via the tuning of the donor strength, modifying the substituents about the triazine, varying the nature of the D–A bridge and switching CT channels (intramolecular CT vs. through-space CT). The plethora of examples contained within this review reveals the versatility of triazine as an acceptor in the design of TADF emitters. By simply varying the strength and number of donors along with the structure of the bridging aryl groups, the emission spectrum can be easily tuned from deep blue through to yellow. The planar conformation adopted by the TRZ moiety can facilitate to the formation of intermolecular exciplexes or through space charge transfer interactions, which enriches the photophysical behavior of these compounds and can contribute to enhancing $k_{\text{RISC}}$.

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### Table 20. Summary of device structures and performance.

| Emitter | Device Structure | EL$_{\text{max}}$ [nm] | CIE | $V_{\text{on}}$ [V] | EQE/PE/CE$^{\text{EQ}}$ [%/lm W$^{-1}$/cd A$^{-1}$] | EQE100/1000 [cd] [m$^{-2}$] | Ref. |
|---------|-----------------|-------------------------|-----|------------------|---------------------------------|-------------------------------|-----|
| DMAC–TRZ | ITO/PEDOT:PPS/TAPTAP/cP/mCPCN:DMAC–TRZ 8 wt%DPSS/3TPyMB/LiF/Al | ≥500 | – | 3 | 26.5/65.6/66.8 | 25.1/122.0 | [91] |
| DMAC–TRZ | ITO/MoO3/TAPTAP/mCPCN: DMAC–TRZ 8 wt%DPSS/3TPyMB/LiF/Al | ≥505 | – | 3 | 27.4/80.8/77.1 | 25.8/22.4 | [91] |
| PXZ–TRZ | ITO/α–NPD/6 wt% PXZ–TRZ: CBP/TPB/LiF/Al | ≥520 | – | 3.5 | 12.5/—/— | –/– | [91] |
| PTZ–TRZ | ITO/α–NPD/2 wt% PTZ–TRZ: CBP/TPB/LiF/Al | ≥532 | – | 3.5 | 10.8/—/— | –/– | [91] |
| 3ACR–TRZ | ITO/PEDOT:PPS/16 wt% 3ACR–TRZ:CBP/BmPyPhBr/LiF/Al | ≥530 | – | 3.5 | 15.1/17.4/15.6 | –/– | [96] |
| tri–PXZ–TRZ | ITO/α–NPD/6 wt%: mCBP/TPB/LiF/Al | ≥550 | – | 3.5 | 13.3/—/— | –/– | [97] |
| TRZ3(Ph–PTZ) | ITO/α–NPD/TCTA/mCPCN:12 wt% TRZ3(Ph–PTZ):mCBP/DPEPO/TPB/LiF/Al | ≥550 | (0.23, 0.75) | 4.2 | 17.4/17.4/58.6 | –/– | [95] |
| i–DMAC–TRZ | ITO/TAPTAP/10 wt% i–DMACTRZ: mCPCN:TmPyPB/LiF/Al | ≥500 | – | 3 | 25.8/62.7/60 | 24.1/18.3 | [100] |
| DPAC–TRZ | ITO/MoO3/TAPTAP/mCPCN:12 wt% DPAC–TRZ:LiF/Al | ≥500 | – | 3 | 25.8/62.7/60 | 24.1/18.3 | [102] |
| SpiroAC–TRZ | ITO/MoO3/TAPTAP/mCPCN:12 wt% SpiroAC–TRZ:LiF/Al | ≥500 | – | 3 | 36.7/98.4/94 | 34.9/30.5 | [102] |
| DTPDDA | ITO/4 wt% ReO3:mCPC/mCPC:TSP01:16 wt% DPTDDA(0.42:0.42:0.16 in wt%):TSP01/4 wt% Rb2CO3:TSP01/Al | ≥450 | (0.149, 0.197) | 3 | 22.3/30.4/35.6 | ≤15.0/10.6 | [106] |
| a–DMAC–TRZ | ITO/TAPTAP/mCPC:DPEPO/20 wt% a–DMAC–TRZ:DPEPO/TmPyPB/LiF/Al | ≥505 | (0.18, 0.35) | 3 | 28.9/—/63.7 | 12.7/3.6 | [104] |
| DTPPDDA | ITO/4 wt% ReO3: mCPC/mCPC: TSP01:4 wt% emitter:TSP01/4 wt% Rb2CO3: TSP01/Al | ≥450 | (0.151, 0.087) | 3 | 4.7/—/— | 2.2/— | [107] |
| DTPSAF | ITO/6 wt% ReO3:mCPC/mCPC:10 wt% TSP01/6 wt% Rb2CO3:TSP01/Al | ≥460 | (0.143, 0.131) | 4.1 | 5.7/6.9/ | ≈3.0/— | [101] |
| DTTSAF | ITO/6 wt% ReO3:mCPC/mCPC:10 wt% TSP01/6 wt% Rb2CO3:TSP01/Al | ≥448 | (0.147, 0.096) | 4.1 | 6.2/4.8/ | ≈5.0/— | [101] |
| DTXSAF | ITO/6 wt% ReO3:mCPC/mCPC:10 wt% TSP01/6 wt% Rb2CO3:TSP01/Al | ≥444 | (0.149, 0.082) | 4.1 | 7.7/5.2/ | ≈5.0/— | [101] |
| MA–TA | ITO/PEDOT:PPS/PVK/10 wt% MA–TA:CzSi: TSP01/TPB/LiQ/Al | ≥465 | (0.15, 0.19) | 5.1 | 22.1/—/— | ≈15.0/— | [105] |
| FA–TA | ITO/PEDOT:PPS/PVK/10 wt% FA–TA:CzSi: TSP01/TPB/LiQ/Al | ≥452 | (0.15, 0.13) | 5.5 | 11.2/—/— | –/– | [105] |
| PA–TA | ITO/PEDOT:PPS/PVK/10 wt% PA–TA:CzSi: TSP01/TPB/LiQ/Al | ≥451 | (0.15, 0.10) | 5.5 | 6.7/—/— | –/– | [105] |
Despite the progress that has been made, the potential of triazine as a moiety in TADF emitter design still has not been fully realized. First, one of the major factors affecting the device lifetime of OLEDs is the stability of the emitter. TADF compounds containing a TRZ acceptor have already demonstrated some potential for improved device lifetimes over their analogs containing acceptors like benzophenone or diphenyl sulfone. TRZ has long been recognized as a chemically stable moiety in the design of epoxy resin,[108] polymers,[109] and covalent TRZ frameworks (CTFs);[110] however, OLED stability studies based on TRZ-functionalized TADF emitters remain limited. Studies that probed the influence of intramolecular hydrogen bonding, glass transition temperatures, and charge mobility on the stability of TRZ-functionalized molecules and the impact on the device lifetime would be welcome.

The orientation of the TDM of the emitters, which impacts the light out-coupling efficiency of the device, is correlated with the EQE of the OLED. Due to the rigid and planar structure of TRZ linked to extended donors, a number of TRZ-based compounds have been documented to show preferential horizontal orientation of their TDM, leading to enhanced light outcoupling efficiency in the device, with EQEmax > 30%. The parameters controlling the orientation of the TDM during thermal evaporation remain unclear,[111] and this is clearly a design feature that can be exploited further.

Solution-processing techniques such as ink-jet printing are promising for producing large-area OLEDs, which remains challenging and expensive for thermal evaporation. More and more attention has been paid to the development of TRZ-containing TADF dendrimers and polymers as attractive classes of emitters suitable for solution-processed OLEDs. However, in contrast to the advances reported for small molecular weight TADF emitters that show high PLQY, horizontal orientation of their TDM, fast RISC rates, and examples of chiral analogs that show CPL, it remains challenging to develop TADF dendrimers and polymers inheriting these properties. Thus, the performance of RISC rates, and examples of chiral analogs that show CPL, it remains challenging to develop TADF dendrimers and polymers inheriting these properties. Thus, the performance of solution-processed OLEDs containing TRZ-based macromolecules still lags behind small-molecule TRZ-based evaporated OLEDs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbazole, emitters, organic light-emitting diodes (OLEDs), thermally activated delayed fluorescence (TADF), triazine
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