Recent progress of green thermally activated delayed fluorescent emitters

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ABSTRACT
Pure organic-based thermally activated delayed fluorescent (TADF) emitters have been studied for the last five years because of their potential as high-efficiency emitters comparable to phosphorescent emitters. Although the initial external quantum efficiency (EQE) of the TADF emitters was much lower than that of phosphorescent emitters, the current EQE of the TADF organic light-emitting diodes (OLEDs) is quite similar to that of phosphorescent OLEDs. In particular, the EQE of the green TADF OLEDs is already over 30% with the help of the new molecular design fully harvesting triplet excitons of the TADF emitters for light emission through the up-conversion process. In this work, the progress of the device performances of the TADF OLEDs was studied by reviewing the green TADF emitters that had been developed in the last five years.

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1. Introduction
Thermally activated delayed fluorescent (TADF) emitters are becoming very popular because of their high external quantum efficiency (EQE) due to their efficient radiative transition process assisted by the up-conversion process of triplet excitons. In common fluorescent emitters, the triplet excitons generated by the carrier injection process are useless because of their non-radiative nature due to the prohibited triplet-to-singlet radiative transition based on the spin selection rule. The non-radiative triplet excitons, however, can be converted to singlet excitons in the TADF emitters through the reverse intersystem crossing process induced by the weak spin-orbit coupling and the small singlet–triplet energy gap (ΔE_ST) in specially designed donor–acceptor structures [1]. Therefore, all singlet and triplet excitons can be converted to photons for light emission, and enable the maximum theoretical efficiency in the TADF devices [2,3].

There has been much progress in the EQE of the red, green, and blue TADF devices for the last five years, and the most significant advances were made in the green TADF devices because of the relatively easy molecular design of the green TADF emitters. The development of the red TADF emitters was relatively difficult due to the exciton loss mechanism of the energy gap law, while the blue TADF emitters suffer from a large ΔE_ST due to the weak donor and acceptor strength of the building units.

In this work, the chemical structures and device performances of the green TADF emitters were covered based on the literature data reported for the last couple of years to provide a guideline for the development of high-efficiency TADF organic light-emitting diodes (OLEDs) as the device performances of the green TADF emitters are quite similar to those of the green phosphorescent emitters. The relationship between the chemical structures and the various material parameters is discussed, and their effect on the device performances is also described.

2. Molecular design of green TADF emitters
The green TADF emitters generally have peak emission wavelengths of around 500 nm and are the most widely developed emitters among the red, green, and blue emitters because of their high EQE and easy molecular design. They are potentially advantageous for realizing a high EQE compared to that of a red TADF emitter because the non-radiative decay process can be reduced by a high emission energy according to the energy gap law [4]. In the case of the red TADF emitters, a small singlet energy of the red TADF emitters brings about non-radiative decay and a reduced EQE of the red TADF devices. For obtaining a high EQE, the green TADF emitters are also better than the blue TADF emitters because the TADF...
emission can be easily harvested and optimized by various host materials. In the case of the blue TADF emitters, the limited availability of high-triplet-energy host materials makes it difficult to fully activate and optimize the TADF emissions of the blue emitters. Therefore, the best EQE of the green TADF OLEDs (31.2%) was much higher than that of the red (17.5%) and blue (25.0%) TADF OLEDs [5–7].

A general design rule underlying the molecular backbone structure of the green TADF emitters is to combine the donor and acceptor moieties in several different ways. They can be directly linked or connected through an aromatic linker for a high photoluminescence quantum yield (PLQY) and a small ΔEST, which are the most important material characteristics of the TADF emitters.

The basic design platform of the green TADF emitters was not different from that of the red or blue TADF emitters, and the simple management of the degree of conjugation and the donor–acceptor strength could control the emission color. For example, the para-connection rather than meta-connection of the aromatic units and the increases in the number of donor moieties could manage the color from blue to green. The green TADF emitters in this work cover the wavelength range from 480 to 560 nm, which includes the bluish- and yellowish-green emitters.

2.1. cyano (CN)-modified TADF emitters

The most well-known green TADF emitter is 2,4,5,6-tetrakis(3,6-di-tert-butyl-9H-carbazol-9-yl)isophthalonitrile (4CzIPN), with four carbazole donor units and a 1,3-dicyanobenzene acceptor [1]. Three isomers with 1,2-dicyanobenzene (4CzPN), 1,3-dicyanobenzene (4CzIPN), and 1,4-dicyanobenzene (4CzTPN) were compared, and a high EQE (19.2%) was achieved in the 4CzIPN by widely dispersing the highest occupied molecular orbital (HOMO) over the donor moieties, which is helpful for a high PLQY. A high PLQY of above 90% and a relatively short excited-state lifetime of 5.1 μs for delayed emission were reported using the 4CzIPN emitter. After the demonstration of a high EQE close to 20% using the organic 4CzIPN TADF emitter for the first time, several works optimizing the device structure of the 4CzIPN TADF OLEDs followed and reported an improved EQE surpassing the EQE obtained by Adachi et al. Several bipolar host materials with a triplet energy high enough for both the singlet and triplet harvesting of 4CzIPN were proven to be better than the carbazole-type host materials and provided EQEs higher than 20% [8–17]. In particular, 3-(3-(carbazole-9-yl)phenyl)pyrdo[3′,2′:4,5]furo[2,3-b]pyridine (3CzPFP) was the best host material of 4CzIPN and realized the best EQE of 31.2% in the 4CzIPN devices [6]. A mixed host of hole- and electron-transport-type host materials also worked effectively as the host of 4CzIPN [17–20]. Several mixed host systems made up of carbazole-type hole transport hosts and phosphine-oxide or pyridine-type electron transport hosts were developed through the proper selection of host materials based on the energy levels, carrier transport properties, and triplet energy [17,18]. All the mixed hosts provided a high EQE of above 20%, and the highest EQE of the 4CzIPN device that was obtained using the mixed host was 29.6% [18].

The 4CzIPN dopant was originally reported as a vacuum-evaporable TADF emitter, but it was also applied as a soluble emitter for solution-processed TADF OLEDs [21–23]. Although the 4CzIPN dopant has a high molecular weight, the distortion of the carbazole units by the steric hindrance rendered 4CzIPN soluble in polar solvents. 4CzIPN was poorly soluble in aromatic solvents, and showed a low EQE in the solution-processed OLEDs, but it could provide a high EQE through processing in a polar solvent, due to the improved solubility [24]. The poor processing problem of 4CzIPN could be solved by introducing tert-butyl-modified carbazole in place of carbazole, and a 2,4,5,6-tetrakis(3,6-di-tert-butyl-9H-carbazol-9-yl)isophthalonitrile (t-4CzIPN) TADF emitter could show similar EQEs in the vacuum-deposited and solution-processed devices [24]. Methyl-modified 2,4,5,6-tetrakis(3,6-dimethyl-9H-carbazol-9-yl)isophthalonitrile (m-4CzIPN) did not help improve the solubility of 4CzIPN.

In addition to its high EQE and versatile processing in different fabrication processes, 4CzIPN could provide long-term stability in the green devices [25]. The 4CzIPN emitter was evaluated as a stable green emitter compared with the conventional green phosphorescent emitter, and exhibited a longer lifetime than the phosphorescent emitter, which confirmed that the TADF emitters could replace the current phosphorescent emitters in practical applications.

The success of 4CzIPN as a green TADF emitter motivated researchers to design various TADF emitters with a CN functional group. A combination of three CN groups and three triphenylamine donors provided 4,4′-bis(diphenylamino)-5′-(4-(diphenylamino)phenyl)-[1,1′:3′, 4′-terphenyl]-2′,4′,6′-tricarbonitrile (3DPA3CN) with a high PLQY of 100% under nitrogen [26]. Although the excited-state lifetime for the delayed emission of 3DPA3CN was very long (550 μs), the high PLQY resulted in a high EQE of 21.4% in the TADF device. The 1,2-dicyanobenzene-based compounds 4,5-bis(5H-benzofuro[3,2-c]carbazol-5-yl)phthalonitrile (BFCz-2CN) and 4,5-bis(5H-benzofuro[4,5]thieno[3,2-c]carbazol-5-yl)phthalonitrile (BTCz-2CN) were also green TADF emitters.
with CN functional group-based acceptors [27]. Benzofluorocarbazole and benzothienocarbazole were donors of BFCz-2CN and BTCz-2CN, respectively, instead of carbazole, to shift the emission color to longer wavelengths. The emission wavelength of the device was 486 nm, and the EQE of the devices was around 12%. The 1,2-dicyanobenzene moiety was also an acceptor of the 4,4′′-bis(9,9-dimethylacridin-10(9H)-yl)-[1,1′:2′,1″-terphenyl]-4′,5′-dicarbonitrile (Ac-VPN) and 4,4″-di(10H-phenoxazin-10-yl)-[1,1′:2′,1″-terphenyl]-4′,5′-dicarbonitrile (Px-VPN) green emitters [28]. The acceptor moiety was modified with donor moieties via a phenyl linker, instead of the direct substitution of the donor moiety. The device performances of the Ac-VPN devices revealed that the phenyl-linker-based design strategy was better than the linker-free design in terms of attaining a high EQE through the high oscillator strength due to the HOMO–lowest unoccupied molecular orbital (LUMO) overlap in the phenyl linker.

The dicyanobenzene and 3,3-bicarbazole-based emitters 5,5′-(9H,9′H-[3,3′-bicarbazole]-9,9′-diyl)diisophthalonitrile (35IPNDCz) and 2,2′-(9H,9′H-[3,3′-bicarbazole]-9,9′-diyl)diisophthalonitrile (26IPNDCz) were also green TADF emitters [29]. The effect of the CN position on ΔEST and the delayed fluorescence lifetime of the TADF emitters was studied. 2,6 Modification was found to be effective for reducing the ΔEST and the fluorescence lifetime delay due to the large distortion between the donor and acceptor units assisting the charge transfer (CT) complex formation and HOMO–LUMO separation. The EQE of the devices, however, was less than 10% in the two devices. 5-(9′H-[9,9′-6,9″-tercarbazol]-9′-yl)isophthalonitrile (DCN3) was also an emitter with the 3,3-dicyanobenzene acceptor and the 3,6-dicarbazolylcarbazole donor [30]. In spite of the small ΔEST of 0.13 eV, the low PLQY of 0.39 resulted in a moderate EQE of 13.3%. Other than the compounds explained above, benzonitrile-type compounds were also synthesized. As benzonitrile is a weak acceptor unit, a strong donor or multiple donors were attached to develop the TADF emitters. 4,4′-(Phenazine-5,10-diyl) dibenzonitrile (DHPZ-2BN) was a derivative of the benzonitrile moiety with a strong phenazine donor, but showed a low EQE of 6.0% in the device [31]. On the other hand, the benzonitrile derivatives, such as 2,3,4,5,6-penta-(9H-carbazol-9-yl)benzonitrile (5CzBN) and 2,3,4,5,6-pentakis-(3,6-di-tert-butyl-9H-carbazol-9-yl)benzonitrile (5TCzBN) with five carbazole-based donors, performed much better than DHPZ-2BN by realizing high EQE values of 16.7 and 21.2%, respectively [32]. The comparison of 5CzBN with DHPZ-2BN clearly suggested that the multiple-donor-based design is superior to the strong-donor-based design in terms of the efficient harvesting of the excitons of the TADF emitters. In particular, the 5CzBN and 5TCzBN emitters could function as stable emitters to extend the lifetime of the TADF emitters because their molecular structure is made up of stable benzonitrile and carbazole units.

Another approach that was employed for the utilization of the CN-based acceptor moieties was to apply a CN-modified pyridine moiety as the acceptor unit of the donor–acceptor structure to strengthen the accepting character. 2,6-Di(9H-carbazol-9-yl)-4-phenylpyridine-3,5-dicarbonitrile (CPC) is a green emitter with a 4-phenylpyridine-3,5-carbonitrile moiety as the acceptor and two carbazole units as the donor [33]. The strong electron acceptor decreased the ΔEST up to 0.04 eV, and increased the EQE up to 21.2%, demonstrating the superiority of the 4-phenylpyridine-3,5-carbonitrile as the acceptor of the TADF material design.

Although several TADF emitters with CN-based cyanobenzene or dicyanobenzene acceptors have been reported, they could not reach the EQE level of 4CzIPN. Therefore, a new design approach involving a dual-emitting core design to enhance the device performances of the CN-type TADF emitters was developed by coupling two TADF emitters [34]. The main purpose of the dual-emitting core design was to intensify the absorption of the emitters so as to gain a high PLQY for the TADF emitters. Increases in the absorption coefficient and PLQY were observed through the coupling of two TADF emitters (3,3′,5,5′-tetra(9H-carbazol-9-yl)-[1,1′-biphenyl]-2,2′,6,6′-tetracarbonitrile (DDCzIPN)) [34], and a high EQE of 18.9% was reported compared to 16.4% for each TADF unit [35]. Additionally, the emission wavelength was shifted to a longer wavelength through the extension of the conjugation as two aromatic moieties were directly coupled. Therefore, the dual-emitting core design was effective at controlling the emission color and at enhancing the light absorption and the PLQY.

Similarly, 6,6′-(9H,9′H-[3,3′-bicarbazole]-9,9′-diyl)bis (4-(9H-carbazol-9-yl)isophthalonitrile) (33TCzPN) was developed by coupling 4,6-di(9H-carbazol-9-yl)isophthalonitrile (DCzIPN) via the 3- position of the carbazole donor instead of the phenyl linker [36]. Compared with the DCzIPN emitter, the emission wavelength of the 33TCzPN emitter appeared at a long wavelength because of the intensified donor strength through the coupled carbazole moieties. The absorption coefficient and PLQY were increased by the dual emitter design, while the ΔEST was reduced by the coupled donor design. As a result, a high EQE of 17.9% was obtained. Moreover, the management of the coupling position of carbazole could control the emission color, while maintaining the merits of the dual emitter design: improved absorption and
PLQY. A molecular design involving the connection of the two carbazole moieties via the 3,4- and 4,4-positions improved the EQE up to 21.8 and 19.5%, respectively, while keeping the color coordinate of the decoupled DCzIPN emitter. The same design concept was proven to be successful in the molecular design of triazine-derived emitters, such as 9,9′-bis((4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H,9′H-3,3′-bicarbazole (33TCzTTrz) [37].

Other than the approaches just described, the modification of fluorene with the CN units followed by combination with donors could produce 10-phenyl-10H-spiro[acridine-9,9′-fluorene]-2′,7′-dicarbonitrile (ACR-FLCN) and 2′,7′-bis(di-p-tolylamino)-9,9′-spirobi[fluorene]-2,7-dicarbonitrile (spiro-CN) as green emitters [38–40]. The CN-modified fluorene was connected to the donor moieties through sp [3] carbon, which led to the complete separation of the HOMO and LUMO with a small overlap. A moderate EQE of 12.2% in ACR-FLCN and a low EQE of 4.4% in the spiro-CN devices were achieved because the HOMO and LUMO were completely separated, without any overlap.

The chemical structures, photophysical parameters, and device performances of the CN-modified acceptor-based green TADF emitters are presented in Tables 1 and 2.

### 2.2. Triazine-modified TADF emitters

In addition to the CN-modified aromatic acceptors, one of the most popular acceptor units of the green TADF emitters is heterocyclic triazine, which has been known as a moderate and stable electron acceptor. The triazine moiety was substituted with various donor moieties to develop highly efficient TADF emitters. One of the early triazine derivatives is 12,12′-(6-((1′,1′-biphenyl)-4-yl)-1,3,5-triazine-2,4-diyl)bis(11-phenyl-11,12-dihydroindolo[2,3-a]carbazole) (PIC-TRZ), which has two indolocarbazole units as donor moieties [2,41]. A small ΔEST of 0.11 eV and a high fluorescent decay rate were described, but the EQE of the PIC-TRZ device was only 7.7%, and the delayed fluorescence lifetime was 230 μs. The low EQE and long excited-state lifetime could be overcome by rearranging the indolocarbazole to possess a ΔEST of close to 0 eV. The proper arrangement of the indolocarbazole moiety separated the HOMO and LUMO, which greatly decreased the ΔEST and increased the fluorescent decay rate. 12-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (PIC-TRZ2), which showed a small ΔEST of 0.02 eV and a short TADF lifetime of 2.7 μs, enhanced the EQE of the TADF device up to 14.0% [42]. The 9,9′-(6-phenyl-1,3,5-triazine-2,4-diyl)bis((9H-3,9′-bicarbazole)) (CC2TA) with a carbazolylcarbazole instead of an indolocarbazole also exhibited a reduced ΔEST and a short lifetime, which resulted in a moderate EQE of 11% in the devices [43,44]. Other than the aforementioned compounds, 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9′-phenyl-9H,9′H-3,3′-bicarbazole (CzT) with 3,3-bicarbazole as a donor unit was also reported, but the EQE of the TADF device was only 6% [45].

In the initial development of the triazine-based TADF emitters, the donor moieties were directly connected to the triazine acceptor without any linker to maximize the HOMO and LUMO separation for a small ΔEST. The extensive HOMO and LUMO separation, however, had a negative effect on the EQE of the device because the PLQY of the emitters was low due to the small HOMO and LUMO overlap for radiative decay. This prompted the design of the TADF emitters that possessed an aromatic linker between the donor and acceptor moieties. The aromatic linker plays the role of managing the HOMO and LUMO distribution of the TADF emitters and the corresponding light-emitting properties of the TADF emitters. Generally, the insertion of the aromatic linker reduces the HOMO–LUMO spatial separation, resulting in a HOMO–LUMO overlap at the aromatic linker. Therefore, the oscillator strength and PLQY are improved by the aromatic linker, but the ΔEST and TADF lifetime are damaged. 10-(4-(4,6-Diphenyl-1,3,5-triazin-2-yl)phenyl)-10H-phenoxazine (PXZ-TRZ) is an initial TADF emitter with a phenyl linker between a phenoxazine donor and a diphenyltriazine acceptor [46,47]. A large HOMO–LUMO overlap was induced by the phenyl linker, and a small ΔEST was achieved by the strong phenoxazine donor. The EQE of the PXZ-TRZ TADF device was 12.5%, which was higher than that of the TADF device without the phenyl linker. 10,10′-(6-Phenyl-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene)bis(10H-phenoxazine) (bis-PXZ-TRZ) and 2,4,6-tris(4-(10H-phenoxazin-10-yl)phenyl)-1,3,5-triazine (tri-PXZ-TRZ) were also synthesized based on the phenyl linker design, and the tri-PXZ-TRZ displayed a high EQE of 13.3%, along with a short lifetime of 1.1 μs [47]. After the demonstration of the phenyl linker effect on the performances of the TADF OLEDs using the PXZ-TRZ series, several triazine derivatives with the phenyl linker were reported. Phenothiazine was used instead of phenoxazine in the synthesis of 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10H-phenothiazine (PTZ-TRZ) [48], and a triphenylamine-based donor was adopted in the preparation of N1-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-N4,N4-diphenylbenzene-1,4-diamine (DPA-TRZ) [49]. These compounds showed an EQE similar to that of the PXZ-TRZ-type emitters. Other than the compounds explained...
Table 1. Chemical structures and photophysical properties of green TADF emitters with CN-modified acceptor moieties.

| Material   | Structure | HOMO (eV) | LUMO (eV) | $E_{S}/E_{T}$ (eV) | $\Delta E_{ST}$ (eV) | $\Phi_{PL}$ (%) | $\tau$ (μs) | Ref  |
|------------|-----------|-----------|-----------|---------------------|----------------------|----------------|-----------|------|
| 4CzIPN     | –         | −5.8      | −3.4      | –                   | 0.083                | 93.8$^{[a]}$   | 5.1$^{[a]}$ | [1]  |
| 4CzPN      | –         | –         | –         | 74.4$^{[b]}$        | 13.9$^{[b]}$        | –             | –         | –    |
| 4CzTPN     | –         | –         | –         | 71.6$^{[b]}$        | 1.9$^{[b]}$         | –             | –         | [1]  |
| t-4CzIPN   | –         | –         | –         | 2.43/2.38           | 0.05                 | 78$^{[a]}$     | 3.2$^{[a]}/2.9^{[b]}$ | [24] |
| m-4CzIPN   | –         | –         | –         | 2.40/2.39           | 0.01                 | 67$^{[a]}$     | 2.6$^{[a]}/2.6^{[b]}$ | [24] |
| 3DPA3CN    | –         | –         | –         | 2.32/2.31$^{[b]}$   | 0.01$^{[b]}$         | 82$^{[a]}/100^{[b]}$ | 550$^{[b]}$ | [26] |
| BFCz-2CN   | −6.19     | −3.58     | 2.59/2.46 | 0.13                | 94.6$^{[a]}/85^{[b]}$ | 2.60 | –         | [27] |
| BTCz-2CN   | −6.17     | −3.58     | 2.63/2.46 | 0.17                | 94$^{[a]}/85^{[b]}$  | 1.98 | –         | [27] |
| Ac-VPN     | −5.8      | −3.1      | 2.90/2.70$^{[b]}$ (onset) | 0.20                | 59$^{[a]}/86^{[b]}$  | 5.1 | –         | [28] |
| Px-VPN     | −5.7      | −3.3      | 2.64/2.56$^{[b]}$ (onset) | 0.08                | 42$^{[a]}/77^{[b]}$  | 2.3 | –         | [28] |
| 35IPNDCz   | –         | –         | 2.63/2.49 | 0.14                | 50$^{[a]}/58^{[b]}$  | 145$^{[a]}$  | –         | [29] |
| 26IPNDCz   | –         | –         | 2.54/2.48 | 0.06                | 72$^{[a]}/72^{[b]}$  | 9.2$^{[a]}$  | –         | [29] |
| DCN3       | −5.57     | −2.31     | 2.57/2.44$^{[c]}$ (onset) | 0.13$^{[c]}$        | 39$^{[a]}$          | 3.26 | –         | [30] |
| DHPZ-2BN   | −5.34     | −3.02     | 2.29/2.19$^{[b]}$ (onset) | 0.10$^{[b]}$        | 8.4$^{[a]}/35.2^{[b]}$ | 1.8$^{[a]}/7^{[b]}$ | –         | [31] |
| 5CzBN      | −5.55     | −2.74     | −2.68     | 0.22                | 70                    | 3.7 | –         | [32] |
| STCzBN     | −5.45     | −2.74     | −2.60     | 0.17                | 86                    | 3.4 | –         | [32] |
| CPC        | −6.25     | −3.47     | 2.77/2.73$^{[b]}$ (onset) | 0.04                | 49.7$^{[b]}$        | 46.6 | –         | [33] |
| DDCzIPN    | −6.40     | −3.88     | 2.60/2.47 | 0.13                | 91.3$^{[a]}$         | 2.8$^{[a]}$  | –         | [34] |

(continued)
### Table 1. Continued.

| Material        | Structure | HOMO (eV) | LUMO (eV) | $\Delta$E$_{S/ET}$ (eV) | $\Phi_E$ (%) | $\tau$ (μs) | Ref        |
|-----------------|-----------|-----------|-----------|--------------------------|--------------|-------------|------------|
| 33TCzTTrz       |           | −5.74     | −3.21     | 3.01/2.76 (onset)         | 0.25         | 87          | 8.4 [37]   |
| ACRFLCN ACRF    |           | −6.07     | −2.53     | 2.68/2.58                 | 0.10         | 67.3 (b)    | 3900 (b)   [38,39] |
| Spiro-CN        |           | –         | –         | –                        | 0.057 (b)    | 27 (b)      | 14 (b) [40] |

Note: [a] Solution. [b] Film. [c] Gaussian calculated data.

### Table 2. Device performances of green TADF organic light-emitting diodes doped with emitters with CN-modified acceptor moieties.

| Material     | Host          | Q.E (%) | C.E (cd/A) | P.E (lm/W) | Color index/Peak wavelength (nm) | Ref |
|--------------|---------------|---------|------------|------------|----------------------------------|-----|
| 4CzIPN       | CBP           | 19.3    | –          | –          | 507                              | [1] |
| 3CzPFP       | CBP           | 31.2    | –          | –          | (0.23, 0.51)                     | [6] |
| DCzDCN       | CBP           | 26.7    | 59.1       | 40.4       | (0.18, 0.46)                     | [8] |
| BCP          | CBP           | 19.1    | –          | –          | –                                | [9] |
| PPO27        | CBP           | 24.2    | –          | 52.0       | (0.20, 0.48)                     | [10]|
| pCzB-2CN     | CBP           | 22.9    | –          | 64.4       | (0.26, 0.55)                     | [11]|
| mCzB-2CN     | CBP           | 26.0    | –          | 71.7       | (0.24, 0.54)                     | [11]|
| oCzB-2CN     | CBP           | 20.9    | –          | 46.6       | (0.24, 0.51)                     | [11]|
| SF33         | CBP           | 20.6    | 65.0       | 51.2       | (0.29, 0.58)                     | [12]|
| SF34         | CBP           | 22.3    | 69.0       | 51.5       | (0.29, 0.58)                     | [12]|
| 3TAPFP       | CBP           | 21.2    | –          | –          | (0.19, 0.43)                     | [13]|
| Spiro-CN     | mCP           | 26.5    | 80.6       | 79         | –                                | [14]|
| DBTTP1       | CBP           | 18.7    | –          | –          | LT80 = over 250 h at 1000 cd     | [15]|
| DBTTP2       | CBP           | 20      | –          | –          | LT80 = 150 h at 1000 cd          | [15]|
| CBP:4CzIPN(10 nm) | CBP       | 23.5    | 74.6       | 90.6       |                                  | [16]|
| CBP:4CzIPN(S5 nm)//CBP(S5 nm) | CBP      | 21.5    | 63.6       | 83.2       |                                  | [16]|
| CBP(S5 nm)//CBP:4CzIPN(5 nm) | CBP    | 25.7    | 83.2       | 106.9      |                                  | [16]|
| 4CN34BCz     | CBP           | 21.8    | –          | –          | (0.21, 0.47)                     | [16]|
| mCP:BmPyPb   | CBP           | 28.6    | –          | 56.6       | (0.21, 0.53)                     | [17]|
| mCP:B3PYMPM  | CBP           | 29.6    | 94.5       | 88.6       |                                  | [18]|
| mCP:SPPO1    | CBP           | 24.2    | –          | 50.5       | (0.20, 0.49)/499                 | [19]|
| mCP:TSPO1    | CBP           | 27.5    | –          | 51.6       | (0.17, 0.43)/491                 | [19,20]|
| CBP/TPBi (ETL) | CBP       | 9.4 (a) | 30         | 20         | –                                | [21]|
| CBP/TPBi (ETL) | CBP       | 9.9 (a) | 33         | 30         | –                                | [21]|
| CBP/B3PyPB (ETL) | CBP   | 15 (a)  | 50         | 51         | –                                | [21]|
| t-4CzIPN     | CBP           | 18.8/18.3(a) | –     | –          |                                  | [22]|
| CPCB         | CBP           | 14.5/9.9(a) | –     | –          |                                  | [22]|
| PEDOT-PSS:PF1//CBP | CBP    | 24 (a)  | 73         | 58         |                                  | [23]|
| mCBP         | CBP           | 14      | 47         | 30.7       | LT90 = 243 h                     | [25]|
| m-4CzIPN     | SiCz          | 17.1/18 | –          | 45.0/42.7 (a)| (0.31, 0.59)                     | [24]|
| m-4CzIPN     | SiCz          | 19.6/8  | –          | 57.1/13.2 (a)| (0.29, 0.57)                     | [24]|
| 3DPA3CN      | DPEPO        | 21.4    | –          | –          | –                                | [26]|
| BFCz-2CN     | mCP          | 12.1    | –          | –          | 486                              | [27]|
| BTCz-2CN     | mCP          | 11.8    | –          | –          | 486                              | [27]|
| Ar-VPN       | mCBP         | 18.9    | 51.7       | 34.1       | (0.23, 0.50)/504                 | [28]|
| Px-VPN       | mCBP         | 14.9    | 45.4       | 26.7       | (0.35, 0.57)/537                 | [28]|
| 35IPNDCz     | DPEPO        | 9.2     | –          | –          | 487                              | [29]|
| 26IPNDCz     | DPEPO        | 9.6     | –          | –          | 501                              | [29]|
| DQN3         | PPT           | 13.3    | 15.26      | 8.14       | (0.20, 0.37)/492                 | [30]|
| DHP2-2BN     | mCBP         | 6       | –          | 40.0       | (0.22, 0.40)                     | [31]|
| 5CzBN        | mCBP         | 16.7    | –          | 56.1       | (0.21, 0.41)                     | [32]|
| 5TCzBN       | mCBP         | 21.2    | –          | 42.8       | (0.20, 0.35)/490                 | [33]|
| CPC           | mCP          | 21.2    | 47.7       | 42.8       | (0.20, 0.35)/490                 | [33]|
| 26DCZPPY     | DPEPO        | 15.5    | –          | –          | (0.23, 0.39)/512                 | [33]|
| DDCzIPN      | mCP:BmPyPb   | 18.9    | 49.4       | 38.3       | (0.22, 0.46)/497                 | [34]|
| 33TCzIPN     | DPEPO        | 17.9    | 51.7       | 38.0       | (0.29, 0.52)/510                 | [36]|
| 33TCzTTrz    | DPEPO        | 25.0    | 64.3       | 57.7       | (0.23, 0.42)/490                 | [37]|
| ACRFLCN (ACRF) | TPSi-F     | 10.1    | –          | –          |                                  | [38]|
|               | PYD2         | 7.7     | –          | –          |                                  | [39]|
|               | CzSi         | 8.4     | –          | –          |                                  | [39]|
|               | DPEPO        | 12.2    | –          | –          |                                  | [39]|
| Spiro-CN     | mCP          | 4.4     | 13.5       | 13.0       | –                                | [40]|

Note: [a] Solution. [b] Film. [c] Gaussian calculated data.
above, 5,10-bis(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-5,10-dihydrophenazine (DHPZ-2TRZ) was known [31], and the solution-processed 2,4,6-tris-(4-‘9”H-[9,3’6’, 9”-tercyclopenta]-9’-yl)phenyl)-1,3,5-triazine (G2TAZ), 2, 4, 6-tris-(4-(6’,6”’-di(9H-carbazol-9-yl)-9’”H-[9,3’,9’,3”’: 6’,9”’-:3’,9’”-quinoxaline-7,10-diyl)bis(N,N-diphenyl-9H-carbazol-3,6-diamine (DACT-II) compound resolved the low EQE issue of the triazine compounds [51]. A diphenylaminocarbazole donor was the key to solving the problem by enabling 100% PLQY and 100% up-conversion efficiency with the help of the close to 0 eV ΔEST and the dipole orientation of the emitter. The maximum EQE of the DACT-II device was as high as 29.6% through just the simple doping of the emitter in the 4,4’-bis(N-carbazolyl)-1,1’-biphenyl (CBP) matrix, which was even higher than that of the 4CzIPN device. The complete up-conversion of the triplet excitons to singlet excitons was a main factor for the high EQE through the small ΔEST by the strong diphenylaminocarbazole donor.

After the initial literatures about the triazine derivatives, great progress was achieved in the device performances by modifying the triazine acceptor with an acridine-type donor moiety. 10-(4-(4,6-Diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (DMAC-TRZ) is one of the best-performing triazine derivatives for the green TADF OLEDs [52,53]. The modification of the triazine moiety with the acridine donor effectively produced a green emitter with a small ΔEST of 0.05 eV, a short excited-state lifetime of 3.6 μs, and an accompanying high PLQY of 0.83 owing to the strong donor power of the acridine moiety. A strong CT character was observed due to the large dihedral angle between the acridine and the acceptor moiety, and the strong donor character of the acridine. A very high EQE of 26.5% was achieved using the DMAC-TRZ emitter, and even the non-doped DMAC-TRZ device exhibited a high EQE of 20% because of the hindered intermolecular interaction by the perpendicularly oriented acridine moiety. Analogously, the indenoacridine-type moiety was also effective as the donor moiety of the triazine derivative (5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-7,7,13,13-tetramethyl-7,13-dihydro-5H-indeno[1,2-b]acridine (TrzIAC)), which provided a high EQE of 20.9% [53]. The indenoacridine donor shifted the emission spectrum to a long wavelength because of the aromatic fluorene moiety. Additionally, the solubility-enhancing effect of the acridine moiety through the perpendicular geometry enabled the development of a soluble triazine compound (2,4,6-tris(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)-1,3,5-triazine (3ACR-TRZ)) [54]. The three-acridine-included backbone structure resulted in an ΔEST of 0.015 eV and a high PLQY of 0.98. The final soluble device provided a high EQE of 18.6%, which is one of the best EQE values of the soluble TADF OLEDs. The chemical structures, photophysical parameters, and device performances of the triazine acceptor-based green TADF emitters are presented in Tables 3 and 4.

2.3. Other acceptor-modified TADF emitters

Pyrazine or pyridine-containing acceptor moieties were also applied to the design of the green TADF emitters. Pyrazine and pyridine moieties have two and one nitrogen atom in the aromatic structure, respectively, and possess a weaker electron-accepting character than triazine. Therefore, they were combined with a strong donor moiety or were extended to a polyaromatic structure for green emission. 1,4-Diazatriphenylene was a polyaromatic derivative of pyrazine and was modified with various donor moieties to develop TADF emitters. Phenoxazine, acridine, carbazole, and diphenylaminocarbazole were attached to the 6,11- or 7,10-position of 1,4-diazatriphenylene [55]. As the electron-accepting character of 1,4-diazatriphenylene was weak, only the phenoxazine (6,11-di(10H-phenoxazin-10-yl) dibenzo[f,h]quinoxaline (APT-PXZ), 7,10-di(10H-phenoxazin-10-yl)dibenzo[f,h]quinoxaline (m-APT-PXZ)), acridine (6,11-bis(9,9-dimethylacridin-10(9H)-yl) dibenzo[f,h]quinoxaline (APT-ACR), 7,10-bis(9,9-dimethylacridin-10(9H)-yl)dibenzo[f,h]quinoxaline (m-APT-ACR)), and diphenylaminocarbazole (9,9’-(dibenzo[f,h]quinoxaline-7,10-diyl)bis(N,N-diphenyl-9H-carbazol-3-amine) (m-APT-CDP)) derivatives behaved as TADF emitters. The substitution position had a minimal effect on the TADF behavior of the 1,4-diazatriphenylene derivatives. The green TADF OLEDs employing ATP-PXZ and m-APT-PXZ could attain an above 12% EQE using carbazole-type host materials. 10-(4-(Quinoxalin-2-yl)phenyl)-10H-phenoxazine (PXZQ) and N3,N3,N6, N6-tetraphenyl-9-(4-(quinolin-2-yl)phenyl)-9H-carbazole-3,6-diamine (DACQ) were green TADF emitters derived from pyrazine-based quinoxaline acceptors [56]. The quinoxaline acceptor has a weak electron-accepting character, so it was merged with a strong electron donor, such as phenoxazine and diphenylaminocarbazole. A phenyl linker was inserted between the quinoxaline acceptor and the donor for HOMO–LUMO overlap, which gave a high EQE of above 10%.

The pyridine-type TADF emitters were 10-phenyl-10H-spiro[acridine-9,5’-cyclopenta[1,2-b:5,4-b’]dipyri-
### Table 3. Chemical structures and photophysical properties of green TADF emitters with triazine-based acceptor moieties.

| Material          | Structure | HOMO (eV) | LUMO (eV) | E_g/E_T (eV) | ΔE_GT (eV) | Φ_L (%) | t (μs)    | Ref  |
|-------------------|-----------|-----------|-----------|--------------|------------|---------|-----------|------|
| PIC-TRZ           | –         | –         | –         | 2.66/2.55     | 0.11       | 35/39   | 230 (multi) | [2,41]|  
| PIC-TRZ2          | –         | –         | –         | –            | 0.02       | 45      | 2.7       | [42] |
| CC2TA             | –         | –         | –         | –            | 0.05       | 62      | 22        | [43,44]|  
| CzT               | –         | –         | –         | 2.46/2.39     | 0.07       | 45.6/39.7 | 42.6     | [45] |
| PXZ-TRZ           | –         | –         | –         | 2.30/2.23     | 0.03       | 29.5/65.7 | 0.676    | [46,47]|  
| bis-PXZ-TRZ       | –         | –         | –         | –            | 64         | 1.330   |           | [47] |
| tri-PXZ-TRZ       | –         | –         | –         | –            | 58         | 1.101   |           | [47] |
| PTZ-TRZ           | –         | –         | –         | 2.30/2.19     | 0.11       | 45/100  |           | [49] |
| DPA-TRZ           | –         | –         | –         | 2.07/2.07     | –          | 2.2/6.6 | 0.1       | [31] |
| DHPZ-2TRZ         | –         | –         | –         | 2.77/2.74     | 0.03       | 94/52   | 0.06      | [50] |
| G2TAZ             | –         | –         | –         | 2.79/2.74     | 0.06       | 100/31  | 4.7       | [50] |
| G3TAZ             | –         | –         | –         | 2.86/2.79     | 0.06       | 94/8.5  | 6.3       | [50] |
| G4TAZ             | –         | –         | –         | 2.48/2.43     | 0.050      | 83      | 3.6       | [52,53]|  
| DACT-II           | –         | –         | –         | –            | 0.01       | 46/101  | –         | [51] |
| DMAC-TRZ TrzAc    | –         | –         | –         | 2.39/2.33     | 0.06       | 97      | 1.6       | [53] |
| TrzIAc            | –         | –         | –         | 2.39/2.33     | 0.015      | 98      | 6.7       | [54] |

Note: [a] Solution. [b] Film. [c] Gaussian calculated data.
Table 4. Device performances of green TADF organic light-emitting diodes doped with emitters with triazine-based acceptor moieties.

| Material  | Host     | Q.E (%) | C.E (cd/A) | PE (lm/W) | Color index/Peak wavelength (nm) | Ref |
|-----------|----------|---------|------------|-----------|----------------------------------|-----|
| PIC-TRZ   | mCP      | 5.3     | -          | -         | -                                | [2] |
| PIC-TRZ2  | DPEPO    | 7.7     | -          | -         | (0.26, 0.43)/506                 | [41]|
| CC2TA     | DPEPO    | 11      | -          | -         | 490                              | [43,44]|
| CzT       | DPEPO    | 6       | 9.7        | (0.23, 0.40)/520 |                                   | [45]|
| PXZ-TRZ   | CBP      | 12.5    | -          | -         | 529                              | [46]|
| bis-PXZ-TRZ | mCBP (200 K) | 11.9    | -          | -         | 530                              | [47]|
| tri-PXZ-TRZ | mCBP | 13.3    | -          | -         | 553                              | [47]|
| PTZ-TRZ   | mCBP     | 10.8    | -          | -         | 532                              | [48]|
| DPA-TRZ   | mCBP     | 13.8    | -          | -         | 548                              | [49]|
| DHPZ-2TRZ | mCBP     | 1       | -          | -         | 617                              | [31]|
| G2TAZ     | Single   | 2.4     | -          | -         | (0.25, 0.49)                     | [50]|
| G3TAZ     | Single   | 3.4     | -          | -         | (0.27, 0.49)                     | [50]|
| G4TAZ     | Single   | 1.5     | -          | -         | (0.23, 0.37)                     | [50]|
| DACT-II   | CBP      | 29.6    | -          | -         | -                                | [51]|
| DMAC-TRZ  | mCPCN    | 26.5    | 66.8       | 65.6      | -                                | [52]|
| TrzAc     | mCP:TPBi | 17.7    | -          | -         | (0.24, 0.51)/500                | [53]|
| TrzAc     | mCP:TPBi | 20.9    | -          | -         | (0.33, 0.57)/511                | [53]|
| 3ACR-TRZ  | CBP      | 18.6    | 36.3       | -         | -                                | [54]|

The success of pyridine as the acceptor unit prompted researchers to apply pyrimidine as the acceptor of the donor–acceptor-type molecular structure. Three pyrimidine derivatives, 4,6-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)pyrimidine (Ac-HPM), 10,10′-((2-phenylpyrimidine-4, 6-diyl)bis(4, 1-phenylene))bis(9, 9-dimethyl-9,10-dihydroacridine) (Ac-PPM), and 10, 10′-(2-methylpyrimidine-4, 6-diyl)bis(4, 1-phenylene)bis(9,9-dimethyl-9,10-dihydroacridine) (Ac-MPM), were designed as the donor–acceptor-type emitters possessing a small ΔEST of below 0.20 eV and a high PLQY of around 0.80 [60]. All the three emitters were efficient as triplet-harvesting emitters, and showed a high EQE of around 20% and a low driving voltage in the device. This work proposed that pyrimidine can be an acceptor unit of the TADF emitters, although its acceptor character is not as strong as that of triazine.

Another electron-accepting moiety for the green TADF emitters is a five-member hetero-ring-based acceptor, which includes benzoazole, benzothiazole, benzoimidazole, benzobis(oxazole), benzobis(thiazole), thiadiazole, oxadiazole, and triazole. Comparing the electron-accepting character of benzoxazole, benzothiazole, and benzoimidazole, the order is benzoxazole > benzothiazole > benzoimidazole. Therefore, the emission wavelength of the TADF emitters can be managed through the choice of the heteroatom of the five-member ring acceptor. 10-(4-(Benzo[d]thiazol-2-yl)phenyl)-10H-phenoxazine (BT), 2,6-bis(4-(10H-phenoxazin-10-yl)phenyl)benzo[1,2-d:4,5-d′]bis(thiazole) (BT2), 10-(4-(benzo[d]oxazol-2-yl)phenyl)-10H-phenoxazine (BOX), 2,6-bis(4-(10H-phenoxazin-10-yl)phenyl)benzo[1,2-d:4,5-d′]bis(oxazole) (cis-BOX2), 2,6-bis(4-(10H-phenoxazin-10-yl)phenyl)benzo[1,2-d:5,4-d′]bis(oxazole) (trans-BOX2) were derived from the five-member ring-type acceptors and a phenoxazine donor, and they showed short TADF lifetimes of less than 1 μs and a small ΔEST of less than 0.1 eV [61]. The cis-BOX2 emitter was the best green TADF emitter among the five emitters, with a high PLQY of 0.98 and a high EQE of 17.6%. 5,10-Bis(4-(10H-phenoxazin-10-yl)phenyl)-5,10-dihydrophenazine (DHPZ-2BTZ) was also a derivative of benzothiazole, although the EQE of the TADF device was only 5% [31]. 5,10-Bis(4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-5,10-dihydrophenazine (DHPZ-2BI) was a benzoimidazole derivative with the benzoimidazole linked with a strong phenazine donor for TADF emission. Even though the ΔEST of DHPZ-2BI was 0.19 eV, due to the weak electron-accepting
character of benzoimidazole, a moderate EQE of 12% was obtained. In the case of the oxadiazole- and triazole-based compounds, such as 2-(phenyl-5-((10H-phenylphenazin-5(10H)-yl)phenyl)-1,3,4-oxadiazole (PPZ-DPO), 5-(4-(4,5-diphenyl-4H-1,2,4-triazol-3-yl)phenyl)-10-phenyl-5,10-dihydrophenazine (PPZ-3TPT), and 5-(4-(3,5-diphenyl-4H-1,2,4-triazol-4-yl)phenyl)-10-phenyl-5,10-dihydrophenazine (PPZ-4TPT), oxadiazole shifted the emission wavelength to longer wavelengths compared to triazole because of the relatively strong electron-accepting character [3]. The oxadiazole compound reduced the $\Delta E_{ST}$ compared to the triazole compounds through combination with phenoxazine, and behaved as an efficient green TADF emitter. The EQE of the benzophenone-derived TADF emitters was slightly improved by adopting benzoylbenzophenone moieties (BPX), and behaved as an efficient green TADF emitter. The EQE of the benzophenone-derived TADF emitters was moderate (6.7%).

The excited-state lifetime was close to 23 $\mu$s, and the EQE of the non-doped TADF OLEDs was moderate (6.7%). The EQE of the benzophenone-derived TADF emitters was slightly improved by adopting benzoylbenzophenone as the acceptor moiety (AcPmBPX and PmBPX) [65]. The large distortion between the benzoylbenzophenone moiety and the donor moieties was induced by the steric hindrance of the bulky benzoylbenzophenone moiety, which led to a small $\Delta E_{ST}$ of less than 0.1 eV and a moderate EQE of 11% in the devices. Other than the compounds, 10-phenyl-10H,10′H-spiro[acridine-9,9′-anthracen]-10′-one (ACR SA) is also known as an aromatic ketone-derived green emitter with a small $\Delta E_{ST}$ of 0.03 eV through the complete separation of the HOMO and LUMO. In spite of the complete isolation of the HOMO and LUMO, a high EQE of 16.5% was reported [66].

Aromatic sulfones were also effective as the acceptor moiety of the green TADF emitter through the appropriate selection of donor moieties. A diphenylsulfone moiety was used as the core in combination with phenazine and phenothiazine to prepare 10,10′-(sulfonylbis[4,1-phenylene])bis(5-phenyl-5,10-dihydrophenazine) (PPZ-DPS) and 10,10′-(sulfonylbis(4,1-phenylene))bis(10H-phenothiazine) (PXZ-DPS) [3]. The assembly of a weak electron-accepting diphenylsulfone moiety with strong electron donors induced green emission, a small $\Delta E_{ST}$ of less than 0.1 eV, a short lifetime of less than 3.1 $\mu$s, and a high PLQY of 0.90. The PXZ-DPS device could realize a high EQE of 17.5% in the green device. Similarly, asymmetric 10-(4-(4-(10H-phenothiazin-10-yl)phenyl)sulfonyl)phenyl)-10H-phenothiazine (PTSOP) and symmetric 10,10′-(sulfonylbis(4,1-phenylene))bis(10H-phenothiazine) (PTSOP) were also evaluated as the TADF emitters [67]. The asymmetric substitution of one phenoxazine and one phenothiazine was tried as a design method for developing high-efficiency, non-doped TADF OLEDs. Aggregation-induced emission behavior instead of exciton quenching was observed in the asymmetrically substituted PTSOP emitter, which resulted in a similar EQE in the doped and non-doped TADF devices. The EQE of the non-doped PTSOP device was 17.0%. On the other hand, the EQE of the symmetrically substituted PTSOP device was degraded in the non-doped device, suggesting the superiority of the asymmetric molecular design for high efficiency in the non-doped device. The EQE of the diphenylsulfone-derived TADF emitters could be further enhanced up to 21.5% by replacing the diphenylsulfone moiety with a thioxanthone moiety. 2-(9-Phenyl-9H-carbazol-3-yl)-9H-thioxanthene-9-one, 10,10-dioxide (TXO-PhCz) and 2-(4-(diphenylamino)phenyl)-9H-thioxanthene-9-one, 10,10-dioxide (TXO-TPA) were synthesized by coupling the thioxanthone moiety with the phenylcarbazole and triphenylamine donor moieties, respectively [68]. The high PLQY and efficient up-conversion of the triplet exciton to a singlet exciton were proposed as the main reasons for the high EQE. In addition, aggregation-induced emission behavior was detected. The thianthrene-9,9′,10,10′-tetraoxide with two sulfone units was quite similar to the thioxanthone acceptor. Two emitters, 2-(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)thianthrene 5,5,10,10-tetraoxide (AC...
Table 5. Chemical structures and photophysical properties of green TADF emitters with acceptor moieties other than CN-modified aromatics and triazine.

| Material    | Structure | HOMO (eV) | LUMO (eV) | $E_r/E_f$ (eV) | $\Delta E_{ST}$ (eV) | $\Phi_{PL}$ (%) | $\tau$ (μs) | Ref   |
|-------------|-----------|-----------|-----------|---------------|----------------------|----------------|-----------|-------|
| ATP-PXZ     |           | -5.6      | -3.1      | 2.76/2.67     | 0.09                 | 24/63          | 1.9       | [55]  |
| m-ATP-PXZ   |           | -5.7      | -3.1      | 2.74/2.70     | 0.04                 | 30/81          | –         | [55]  |
| ATP-ACR     |           | -5.8      | -3.0      | 2.88/2.76     | 0.16                 | 26/49          | –         | [55]  |
| m-ATP-ACR   |           | -5.9      | -3.1      | 2.92/2.79     | 0.13                 | 36/52          | –         | [55]  |
| m-ATP-CDP   |           | -5.7      | -3.1      | 3.02/2.76     | 0.26                 | 77/77          | 18.1      | [55]  |
| PXZQ        |           |           |           | 2.29/2.10     | 0.19                 | 86             | 1200      | [56]  |
| DACQ        |           |           |           | 2.37/2.29     | 0.08                 | 84             | 26        | [56]  |
| A-AF        |           |           |           |               | 0.594               | –              | –         | [57]  |
| DPAA-AF     |           |           |           |               | 0.021               | 70             | 2.4/4.3   | [57]  |
| 4CzCNpy     |           | 5.72      | 3.26      | 2.28/2.21     | 0.07                 | 54.9           | 8.5       | [58,59]|
| Ac-HPM      |           | -5.65     | -2.84     | 2.84/2.66     | 0.18                 | 77             | 21.4      | [60]  |
| Ac-PPM      |           | -5.65     | -2.85     | 2.84/2.65     | 0.19                 | 79             | 20.7      | [60]  |
| Ac-MPM      |           | -5.66     | -2.85     | 2.89/2.70     | 0.19                 | 80             | 26.2      | [60]  |
| BT          |           |           |           |               | 0.07                 | 33/72          | 0.47      | [61]  |
| BT2         |           |           |           |               | 0.05                 | 51/80          | 0.62      | [61]  |
| BOX         |           |           |           |               | 0.07                 | 22/75          | 0.43      | [61]  |
| cis-BOX2    |           |           |           |               | 0.03                 | 62/98          | 0.61      | [61]  |
| trans-BOX2  |           |           |           |               | 0.05                 | 32/81          | 0.59      | [61]  |
| DHPZ-2BTZ   |           | -5.30     | -2.92     | 2.15/2.15     | 0                     | 9.7/33          | 0.24/1    | [31]  |

(continued)
| Material       | Structure | HOMO (eV) | LUMO (eV) | $E_v/E_T$ (eV) | $\Delta E_{ST}$ (eV) | $\Phi_T$ (%) | $\tau$ (μs) | Ref  |
|----------------|-----------|-----------|-----------|----------------|----------------------|--------------|------------|------|
| DHPZ-2BI       | ![DHPZ-2BI](image) | −5.30     | −2.85     | 2.31/2.12<sup>[b]</sup> | 0.19<sup>[b]</sup> | 24.1<sup>[a]/67.6<sup>[b]</sup> | 5.71<sup>[a]/50<sup>[b]</sup> | [31] |
| PPZ-DPO        | ![PPZ-DPO](image) | −4.91     | −2.49     | 2.40/2.31<sup>[a]</sup>/2.46/2.38<sup>[b]</sup> (onset) | 0.07<sup>[a]/0.08<sup>[b]</sup> | 12<sup>[a]/45<sup>[b]</sup> | 0.52<sup>[a]/2.4<sup>[b]</sup> | [3] |
| PPZ-3TPT       | ![PPZ-3TPT](image) | −4.85     | −2.20     | 2.65/2.38<sup>[a]</sup>/2.68/2.38<sup>[b]</sup> (onset) | 0.27<sup>[a]/0.3<sup>[b]</sup> | 7<sup>[a]/42<sup>[b]</sup> | 33<sup>[a]/4900<sup>[b]</sup> | [3] |
| PPZ-4TPT       | ![PPZ-4TPT](image) | −4.85     | −2.06     | 2.80/2.38<sup>[a]</sup>/2.81/2.38<sup>[b]</sup> (onset) | 0.42<sup>[a]/0.43<sup>[b]</sup> | 3<sup>[a]/12<sup>[b]</sup> | 28,000<sup>[b]</sup> | [3] |
| 2PXZ-OXD       | ![2PXZ-OXD](image) | −5.4      | −2.8      | 3.40/2.83<sup>[a]</sup> | 0.15 | 43.1<sup>[b]/87<sup>[c]</sup> | 13.27<sup>[b]/73,249,1420<sup>[c]</sup> | [62,63] |
| bis-PXZ-TDZ    | ![bis-PXZ-TDZ](image) | −5.6      | −3.2      | 2.30<sup>[a]</sup> | 0.11 | 68.5<sup>[b]</sup> | 7,56,311<sup>[b]</sup> | [63] |
| Px2BP          | ![Px2BP](image) | −5.44     | −2.92     | 2.61/2.58<sup>[b]</sup> (onset) | 0.03<sup>[b]</sup> | 44<sup>[a]/70<sup>[b]</sup> | 23<sup>[b]</sup> | [64] |
| p-Px2BBP       | ![p-Px2BBP](image) | −5.62     | −3.13     | 2.59/2.53<sup>[b]</sup> (onset) | 0.06<sup>[b]</sup> | 10<sup>[a]/36<sup>[b]</sup> | 26<sup>[b]</sup> | [64] |
| AcPmBPX        | ![AcPmBPX](image) | −5.80     | −2.90     | 2.79/2.74<sup>[b]</sup> (onset) | 0.05 | 20<sup>[a]/46<sup>[b]</sup> | 925<sup>[b]</sup> | [65] |
| PxPmBPX        | ![PxPmBPX](image) | −5.60     | −2.80     | 2.70/2.82<sup>[b]</sup> (onset) | 0.02 | 10<sup>[a]/57<sup>[b]</sup> | 314<sup>[b]</sup> | [65] |
| ACRSA          | ![ACRSA](image) | −         | −         | − | 0.03<sup>[c]</sup> | 81<sup>[c]</sup> | 5.3<sup>[c]</sup> | [66] |
| PPZ-DPS        | ![PPZ-DPS](image) | −5.10     | −2.69     | 2.40/2.31<sup>[a]</sup>/2.43/2.35<sup>[b]</sup> (onset) | 0.09<sup>[a]/0.08<sup>[b]</sup> | 3<sup>[a]/20<sup>[b]</sup> | 0.28<sup>[a]/1.0<sup>[b]</sup> | [3] |
| PXZ-DPS        | ![PXZ-DPS](image) | −5.59     | −2.79     | 2.71/2.65<sup>[a]</sup>/2.74/2.66<sup>[b]</sup> (onset) | 0.08<sup>[a]/0.08<sup>[b]</sup> | 81<sup>[a]/90<sup>[b]</sup> | 2.5<sup>[a]/3.1<sup>[b]</sup> | [3] |
| PTSOPO         | ![PTSOPO](image) | −5.78     | −3.06     | 2.97/2.88 | 0.09 | 80 | 6.2 | [67] |
| PTSOPT         | ![PTSOPT](image) | −6.11     | −3.34     | 3.02/2.61 | 0.41 | 14 | – | [67] |
| TXO-PhCz       | ![TXO-PhCz](image) | −5.78     | −3.58     | 2.46/2.37<sup>[a]</sup> | 0.09<sup>[a]/0.05<sup>[b]</sup> | 83<sup>[b]</sup> | – | [68] |
| TXO-TPA        | ![TXO-TPA](image) | −5.37     | −3.49     | 2.27/2.23<sup>[a]</sup> | 0.04<sup>[a]/0.073<sup>[b]</sup> | 90.2<sup>[b]</sup> | 78<sup>[b]</sup> | [68] |
| ACRDSO2        | ![ACRDSO2](image) | −5.26     | −2.65     | – | 0.06 | 34<sup>[a]/71<sup>[b]</sup> | 8.3 | [69] |
| PXZDSO2        | ![PXZDSO2](image) | −5.06     | −2.67     | – | 0.05 | 37<sup>[a]/62<sup>[b]</sup> | 5.0 | [69] |

(continued)
Table 5. Continued.

| Material        | Structure | HOMO (eV) | LUMO (eV) | $\Delta E_{ST}$ (eV) | $\Phi_{PL}$ (%) | $\tau$ (μs) | Ref  |
|-----------------|-----------|-----------|-----------|----------------------|-----------------|-------------|------|
| DPO-TXO2        | ![Structure](image1) | -5.37     | -2.61     | 2.84/2.83 (onset)    | 0.01            | –           | 4.61[a]  |
| PXZ-Mes3B       | ![Structure](image2) | -5.5      | -3.1      | -2.40                | 0.071           | 44[a]/92[b] | –    [71] |
| 2DAC-Mes3B      | ![Structure](image3) | -5.4      | -2.26     | -2.51                | 0.058           | 84[a]/100[b]| –    [71] |
| DAC-Mes3B       | ![Structure](image4) | -5.4      | -2.7      | -2.54                | 0.062           | 91[a]/87[b]| –    [71] |
| PrFPCz          | ![Structure](image5) | -5.39     | -2.81     | –                    | 0.06            | 40          | 4.3   [72] |
| PrFCzP          | ![Structure](image6) | -5.44     | -2.72     | –                    | 0.07            | 38          | 2.4   [72] |
| PrFTPAA         | ![Structure](image7) | -5.14     | -2.78     | –                    | 0.04            | 60          | 3.1   [72] |
| 11              | ![Structure](image8) | -5.60     | -2.20     | 2.88/2.85[a] (onset) | 0.028           | 99[b]       | 1.87  [73] |
| 2e              | ![Structure](image9) | -5.5      | -2.57     | 2.52/2.46            | 0.06            | 92[b]       | 31.8[b] [74] |
| HAP-3MF         | ![Structure](image10) | -6.0      | -3.4      | –                    | –               | 26[a]/12.7[b]| 0.5 (EL) |
| AcPI            | ![Structure](image11) | –         | –         | –                    | 0.01[c]         | 50[b]       | 21[b]  [76] |
| AcMI            | ![Structure](image12) | –         | –         | –                    | 0.24[c]         | 43[b]       | –     [76] |

Note: [a] Solution. [b] Film. [c] Gaussian calculated data.

RDSO2) and 2-(4-(10H-phenoxazin-10-yl)phenyl)thianthren 5,5,10,10-tetraoxide (PXZDSO2), functioned efficiently in both the evaporation and solution devices by achieving a high EQE of above 15% as green emitters [69]. Other than the compounds explained above, 9,9-dimethyl-2,7-di(10H-phenoxazin-10-yl)-9H-thioxanthene 10,10-dioxide (DPO-TXO2) with a sulfone-derived 9,9-dimethylthioxanthene-S,S-dioxide acceptor was a green emitter, although the EQE was moderate (13.5%) [70].

Other types of green TADF emitters are the boron compounds, which utilize the strong electron-withdrawing power by the vacant p orbital of the boron atom. Triarylboron is a representative boron-based acceptor moiety for realizing a high EQE in donor–acceptor-type emitters. In the design of the triarylboron-type compounds, alkyl-substituted triarylboron was typically selected as the acceptor unit because of the oxygen and water sensitivity of the boron atom. Trimesitylboron was the acceptor unit of 10-(4-(dimesitylboryl)-3,5-dimethylphenyl)-10H-phenoxazine (PXZ-Mes3B), 9-(4-(dimesitylboryl)-3,5-dimethylphenyl)-N3,N3,N6,N6-tetraphenyl-9H-carbazole-3,6-diamine (2DAC-Mes3B), and 9-(4-(dimesitylboryl)-3,5-dimethylphenyl)-N,N-diphenyl-9H-carbazol-3-amine (DAC-Mes3B) emitters with phenoxazine, bis(diphenylamino)carbazole, and diphenylaminocarbazole, respectively [71]. Among the three emitters, the PXZ-Mes3B emitter performed better than the other emitters in terms of the EQE of the device (22.8%). The order of the EQE of the...
Table 6. Device performances of green TADF organic light-emitting diodes doped with emitters with acceptor moieties other than CN-modified aromatics and triazine.

| Material          | Host     | Q.E (%) | C.E (cd/A) | P.E(lm/W) | Color index/Peak wavelength (nm) | Ref     |
|-------------------|----------|---------|------------|-----------|----------------------------------|---------|
| ATP-PXZ           | CBP      | 11.7    | 37.9       | 24.8      | 529                              | [55]    |
| m-ATP-PXZ         | mCP      | 12.6    | 34.0       | 24.3      | 516                              | [55]    |
| ATP-ACR           | mCP      | 7.5     | 11.5       | 5.7       | 496                              | [55]    |
| m-ATP-ACR         | mCBP     | 8.7     | 13.1       | 6.2       | 486                              | [55]    |
| m-ATP-CDP         | mCP      | 7.5     | 13.4       | 6.4       | 499                              | [55]    |
| PKZQ              | DPEPO    | 10.4    |            | –         | –                                | [56]    |
| DACQ              | DPEPO    | 12.8    |            | –         | –                                | [56]    |
| DPA-AF            | mCP      | 9.6     |            | –         | –                                | [57]    |
| 4CzCNPy           | 4CzPy    | 11.3[a] | 38.9       | 14.8      | (0.34, 0.59)                     | [58]    |
| 4CzCNPy           | mCP      | 12.6    | 34.0       | 24.3      | 516                              | [55]    |
| ATP-ACR           | mCP      | 7.5     | 13.4       | 6.4       | 499                              | [55]    |
| m-ATP-ACR         | mCBP     | 8.7     | 13.1       | 6.2       | 486                              | [55]    |
| m-ATP-CDP         | mCP      | 7.5     | 13.4       | 6.4       | 499                              | [55]    |
| PXZQ              | DPEPO    | 10.4    |            | –         | –                                | [56]    |
| DACQ              | DPEPO    | 12.8    |            | –         | –                                | [56]    |
| DPA-AF            | mCP      | 9.6     |            | –         | –                                | [57]    |
| 4CzCNPy           | 4CzPy    | 11.3[a] | 38.9       | 14.8      | (0.34, 0.59)                     | [58]    |
| DACQ              | DPEPO    | 10.4    |            | –         | –                                | [56]    |
| DPA-AF            | mCP      | 9.6     |            | –         | –                                | [57]    |

The electron-accepting property of the boron atom also allowed the preparation of donor–acceptor-type pyridyl pyrrolide boron complexes as the TADF emitters. The boron atom in the pyridyl pyrrolide boron complexes served as a hub for anchoring the donor and acceptor moieties with little influence on the device followed the relative donor strength of the donor moiety.
electronic properties. Three boron complexes, 5,5-bis(4-(9H-carbazol-9-yl)phenyl)-1,3-bis(trifluoromethyl)-5H-pyrrolo[1′,2′:3,4][1,3,2]diazaborolo[1,5-a]pyridin-6-ium-5-uide (PrFPCz), 5,5-bis(9-phenyl-9H-carbazol-3-yl)-1,3-bis(trifluoromethyl)-5H-pyrrolo[1′,2′:3,4][1,3,2]diazaborolo[1,5-a]pyridin-6-ium-5-uide (PrFCzP), and 5,5-bis(4-(diphenylamino)phenyl)-1,3-bis(trifluoromethyl)-5H-pyrrolo[1′,2′:3,4][1,3,2]diazaborolo[1,5-a]pyridin-6-ium-5-uide (PrFTPA), were synthesized as soluble TADF emitters with a small ΔEST of less than 0.1 eV due to the electron-accepting ability of the boron atom [72]. The solution processing of the boron complexes produced TADF OLEDs with an EQE of 13.6%. Phenoxaborin was also a boron-containing acceptor moiety demonstrating a high EQE of above 20%. Carbazole, acridine, and phenoxazine were the donor units of the compounds 9-(4-(10H-dibenzo[b,e][1,4]oxaborinin-10-yl)phenyl)-9H-carbazole (9), 10-(4-(10H-dibenzo[b,e][1,4]oxaborinin-10-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (10), and 10-(4-(10H-dibenzo[b,e][1,4]oxaborinin-10-yl)phenyl)-10H-phenoxazine (11) with the phenoxaborin acceptor, respectively. The weak carbazole-donor-based compound 9 did not show any TADF property, while the strong acridine- and phenoxazine-based compounds 10 and 11 exhibited efficient TADF emission, along with high EQE values of 15.1 and 22.1%, respectively [73]. In the case of the compounds 10 and 11, the steric hindrance between the phenoxaborin acceptor and the phenyl linker induced the distortion of the molecular structure and a strong CT character. A boron-derived 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene acceptor was similar to the phenoxaborin moiety as the acceptor of the TADF emitter, as reported in the photophysical and device data of 10-(5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)-10H-phenoxazine (2e) [74].

Other than the TADF materials shown above, heptazaphenalene-based 2,5,8-tris(4-fluoro-3-methylphenyl)-1,3,3a1,4,6,7,9-heptaazaphenalene (HAP-3MF) [75], phthalimide-based 5,6-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)-2-methylisoindoline-1,3-dione (AcPI), and maleimide-based 3,4-bis(4′-(9,9-dimethylacridin-10(9H)-yl)-[1,1′-biphenyl]-4-yl)-1-methylpyrrolidine-2,5-dione (AcMI) also emitted green light through a TADF emission process involving the triplet-to-singlet up-conversion channel [76]. The chemical structures, photophysical parameters, and device performances of the green TADF emitters based on acceptors, except for the CN-modified aromatics and triazine, are summarized in Tables 5 and 6.

The overall progress of the EQE of the green TADF emitters is summarized in Figure 1.

3. Summary and outlook

As described above, the green TADF emitters were more efficient than the red TADF emitters, and the green TADF OLEDs already reached the EQE level of the green phosphorescent organic light-emitting diodes (PHOLEDs) by engineering TADF emitters and host materials for the TADF emitters. The main reason for this is the design versatility of the green TADF emitters, which permits the donor and acceptor moieties for the green TADF emitter to be diversely selected based on various combinations, such as strong donor–weak acceptor, weak donor–strong acceptor, and moderate donor–moderate acceptor. The other reason is the minimal emission energy loss because all the emissions were within the visible wavelength range. The infrared emission loss of the red emitters and the UV emission loss of the blue TADF emitter can be avoided in the green emitters, which contributes to the high EQE of the green device. Although a high EQE comparable to that of PHOLEDs was achieved, only several donor and acceptor moieties were applied in the design of the green TADF emitters, and further development of the green TADF emitters for a high EQE and a long lifetime is needed. Particularly, a molecular design guaranteeing a stable lifetime must be developed because few emitters were reported as stable emitters. Among the green emitters, only 4CzIPN and 5CzBN could behave as stable emitters because of the intrinsic instability of the common strong donor moieties, such as acridine, phenoxazine, and phenothiazine, and of the typical acceptor moieties, such as the boron derivatives, sulfone derivatives, ketone derivatives, pyrazine,
and pyridine. Therefore, the green emitters should possess a molecular structure with stable donors mostly derived from carbazole, an aromatic linker, and with stable acceptors mostly derived from CN-modified aromatics or triazine-based moieties, for both a high EQE and a long lifetime.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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