

## REVIEW

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## Sensitized organic light-emitting diodes: towards high efficiency and long lifetimes

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Sensitized organic light-emitting diodes (OLEDs) have received extensive attention in recent years owing to their exciton utilization improvement. Along with the advances in fluorescent, phosphorescent, and thermally activated delayed fluorescent (TADF) OLEDs, a series of highly efficient sensitizers have been designed or selected to match them. Sensitized OLEDs realize dual improvements in efficiency and lifetime with the combination of high exciton utilization sensitizers and high-performance emitters. In this review, we systematically summarize the mechanisms of sensitized OLEDs, including phosphorescent, TADF, and exciplex sensitizers. On the basis of this classification, we further introduce the functions and selection criteria of sensitizers for phosphorescent, TADF, and exciplex-sensitized OLEDs. Finally, we hope that such a review will help researchers to design highly efficient and long lifetime sensitized OLEDs.

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## Introduction

Organic light-emitting diodes (OLEDs) have attracted extensive attention owing to their promising applications in large-area displays and solid-state lighting.<sup>1,2</sup> The first-generation light-emitting materials are fluorescent materials exhibiting high photoluminescence quantum yield (PLQY). However, fluorescence emitting materials can transform only singlet excitons into

photons for light emission, leading to the theoretically highest external quantum efficiency (EQE) of only 5%. The key to improving the EQE of fluorescent OLEDs (FOLEDs) is to utilize 75% of the triplet excitons. In 1998, Ma *et al.* designed and synthesized osmium-based phosphorescent materials.<sup>3</sup> Subsequently, Forrest *et al.* reported effective phosphorescent OLEDs (PhOLEDs) using red-emitting Pt complexes.<sup>4</sup> The PhOLEDs incorporate heavy metals to increase the spin-orbit coupling effect, which facilitates the lowest triplet excited state ( $T_1$ ) to the ground state ( $S_0$ ) transition, resulting in an internal quantum efficiency (IQE) of nearly 100%. However, the blue PhOLEDs are thus far not satisfactory in terms of their lifetime and efficiency.<sup>5</sup> Also, to capture the remaining triplet excitons, Adachi *et al.* proposed the first highly efficient purely organic metal-free thermally activated delayed fluorescence (TADF) material in 2012.<sup>6,7</sup> TADF materials

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also exhibit an IQE of 100% by up-converting triplet excitons into singlet excitons through the reverse intersystem crossing process (RISC). Although the TADF OLEDs show excellent performance, they exhibit a broadband emission originating from their strong intramolecular charge transfer feature. In addition, TADF OLEDs suffer from poor device stability due to the slow decay process.<sup>8</sup> In 2016, the multiple resonance TADF (MR-TADF) materials proposed by Hatakeyama *et al.* effectively addressed the problem of colour purity.<sup>9</sup> MR-TADF materials with narrowband emission have great potential for application in ultrahigh-definition OLED displays. However, serious efficiency roll-off and poor device lifetime have greatly limited their development.<sup>10–12</sup>

Besides light-emitting materials engineering, introducing high exciton utilization materials such as phosphorescent, TADF, and exciplex materials as sensitizers into conventional emitters is an additional method to harvest triplet excitons (Fig. 1). In the sensitized OLEDs, the sensitizers do not emit light but transfer energy to the emitters for radiative decay. The initial application of sensitizers in OLEDs can be traced back to 2000.<sup>13</sup> Forrest *et al.* overcame the theoretical limitations of FOLEDs by doping both phosphorescent and fluorescent materials into the host. After the breakthrough concept of TADF

reported by Adachi *et al.* in 2012, TADF materials have also been exploited as suitable sensitizers. In 2014, Adachi *et al.* proposed a double doping strategy using a wide-energy-gap host, a TADF-assistant dopant, and a fluorescence emitting dopant and observed hyperfluorescence (HF).<sup>14</sup> Almost simultaneously, Duan *et al.* designed materials with small  $\Delta E_{ST}$  as sensitizing hosts for conventional fluorescent dopants, and reported the TADF-sensitized fluorescence (TSF) mechanism.<sup>15</sup> In the following year, the first OLED employing a conventional fluorescent dopant sensitized with a TADF exciplex host was reported by Lee *et al.*<sup>16</sup> The sensitized fluorescent OLEDs doped with phosphorescent sensitizers, TADF assisted dopants/sensitizing hosts, and exciplex hosts broke the theoretical efficiency limits. In addition to being used as sensitizers for fluorescent materials, these high exciton utilization materials can also be used as sensitizers for phosphorescent materials. In 2013, Duan *et al.* first reported on using the TADF material as the host for phosphorescent materials, and fabricated TADF-sensitized phosphorescent (TSP) OLEDs.<sup>17</sup> The TSP OLEDs can simultaneously realize high efficiency, low roll-off, and long lifetimes. Quite recently, the MR-TADF materials, with a high RISC process, high PLQY, and low  $\Delta E_{ST}$  values, have also been considered ideal sensitizers for sensitized devices.<sup>18</sup> TADF-sensitized MR-TADF OLEDs achieve higher efficiency, longer lifetimes, and higher color purity than conventional TADF OLEDs.

Herein, this review describes the mechanisms of phosphorescent, TADF, and exciplex sensitized OLEDs and provides details of the different functions of sensitizers in the corresponding OLEDs, including fluorescent, phosphorescent, and MR-TADF OLEDs. This review also discusses the prospects of the sensitized OLEDs.

## Mechanism of the sensitized OLEDs

In the typical sensitized OLEDs, the light-emitting layer is made up of the host, sensitizer, and emitter. Ideally, all excitons formed on the host are transferred into the sensitizer and then to the emitter. Therefore, efficient energy transfer is essential to improve the performance of sensitized OLEDs. We briefly describe



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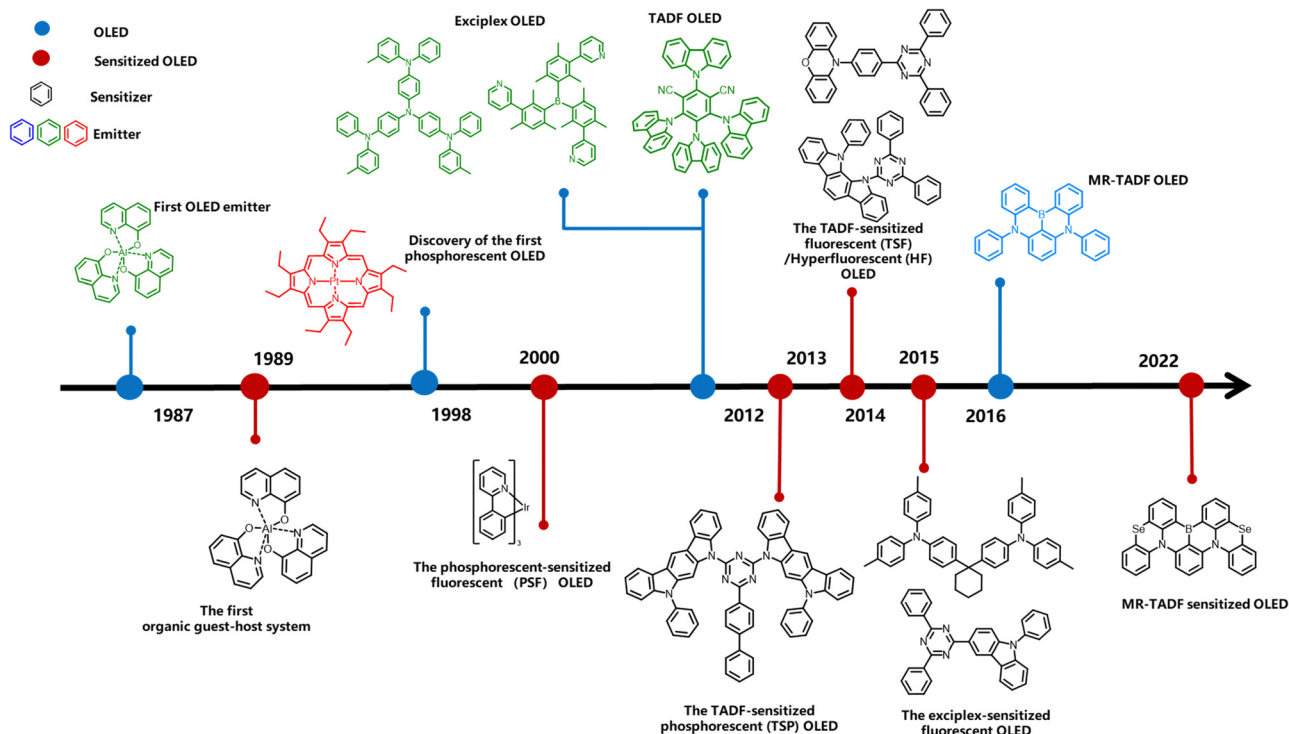


Fig. 1 Milestones in the development of the sensitized OLEDs.

the energy transfer mechanisms, not only the Förster energy transfer (FET) process but also the Dexter energy transfer (DET) process. The FET process is a long-range process through the dipole-dipole interaction in the range of 10–100 Å. The DET process originates from exchange interactions, typically in the range of 5–10 Å.<sup>19,20</sup> To satisfy the optimal FET process from the sensitizer to the emitter, several prerequisites must be thoroughly examined: (i) the photoluminescence (PL) spectrum of the sensitizer should overlap with the absorption spectrum of the emitter, (ii) the emitter should have a high absorption coefficient, (iii) the distance between the sensitizer and the emitter should be relatively close, and (iv) the sensitizer possesses a short-excited state lifetime. In addition to the FET process, the DET process also affects the energy transfer efficiency. The DET process is related to the overlap integral of the spectrum, which is more sensitive to the distance between the sensitizer and the emitter than the FET process. Thus, the DET process can be inhibited by reducing the doping concentration of the emitter or by introducing large blocking groups on the sensitizer and emitter.

Apart from the energy transfer, the formation of excitons on the emitter is also enabled by directing electron-hole recombination, which can be avoided by regulating the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) energy levels or by minimizing the doping concentration of the emitter.<sup>21–23</sup> In this review, it is assumed that excitons are formed in the host and the sensitizer.

### Mechanism of phosphorescence-sensitized OLEDs

Phosphorescent materials assist the emitter in harvesting triplet excitons through a large spin-orbit coupling, making them

effective sensitizers for triplet energy transfer.<sup>13</sup> The schematic diagram of the phosphorescent sensitizer is shown in Fig. 2.

In the sensitized system, following the injection of electrons and holes from the cathode and anode, respectively, the excitons are classified into singlet and triplet excitons that are formed at a ratio of 25 : 75. The initial  $S_1$  and  $T_1$  excitons of the host are transferred to phosphorescent sensitizers *via* the FET and DET processes, respectively. The  $S_1$  excitons will transfer to  $T_1$  *via* an intersystem crossing (ISC) process in phosphorescent sensitizers. The  $T_1$  excitons in sensitizers are transferred to the  $S_1$  of the emitter by the FET process. The most critical step in the cascade energy transfer process is the transfer of energy from triplet excitons of sensitizers to the singlet excitons of the emitter *via* a FET process rather than a DET process. However, the FET rate ( $k_{FET}$ ) between the triplet and the singlet is very slow relative to the transfer

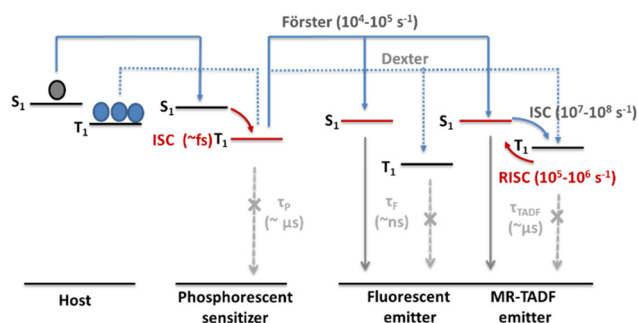


Fig. 2 Diagram of the energy transfer process of the phosphorescence-sensitized system.



between the singlet and the singlet because of the relatively low radiative rate ( $k_r$ ) in the phosphorescent sensitizer. As a result, owing to the high ISC rate ( $k_{ISC}$ ), plenty of excitons will accumulate in the  $T_1$  of the phosphorescent material. Fortunately, the long decay time for the excited phosphorescent triplet state and the PLQY can compensate for the slow  $k_{FET}^{24,25}$

### Mechanism of TADF-sensitized OLEDs

Using TADF materials is an alternative method of harvesting triplet excitons by the RISC process. A schematic diagram of the TADF-sensitized process is shown in Fig. 3.

In a TADF-sensitized system, after excitons formed on the host and transferred to the sensitizer, a part of the singlet excitons can be converted to triplets on the sensitizer by a fast ISC process, followed by the triplet excitons reverting to the  $S_1$  by a relatively slow RISC process. Subsequently, the emitter can harvest the singlet excitons on the TADF sensitizer *via* the FET process. The energy transfer and the radiation decay process of excitons in the fluorescent and TADF emitters are similar to those of the phosphorescence-sensitized system. However, the DET process between the sensitizer and the phosphorescent emitter dominates in the sensitized OLEDs thanks to the nature of phosphorescence emission from the radiative decay of triplet excitons. The RISC process is the key to the energy transfer process in the TADF-sensitized systems. The  $k_{RISC}$  of TADF materials is usually in the range of  $10^5$ – $10^6$   $s^{-1}$ , which is slower than the  $k_{ISC}$  ( $10^7$ – $10^{11}$   $s^{-1}$ ). Therefore, even though the  $k_{FET}$  ( $10^7$ – $10^{11}$   $s^{-1}$ ) of the systems with a TADF sensitizer is faster than that of the phosphorescence-sensitized systems, triplet excitons cannot be utilized in time on account of the slow RISC process.<sup>25</sup>

### Mechanism of exciplex-sensitized OLEDs

An exciplex is an intermolecular charge-transfer excited state formed between a donor and an acceptor, and can facilitate RISC processes and delayed fluorescence.<sup>26</sup> Apart from the RISC process, the delayed fluorescence of the exciplex can also be derived from the triplet–triplet annihilation (TTA).<sup>27</sup> In this review, we only discuss the delayed fluorescence generated by the RISC process. As an effective exciton harvesting approach, the exciplex with the fast RISC process also shows some potential as a sensitizer.

Exciplex acts as a sensitizer by a mechanism similar to the TADF sensitizer. The  $T_1$  exciton can be transferred to  $S_1$  through

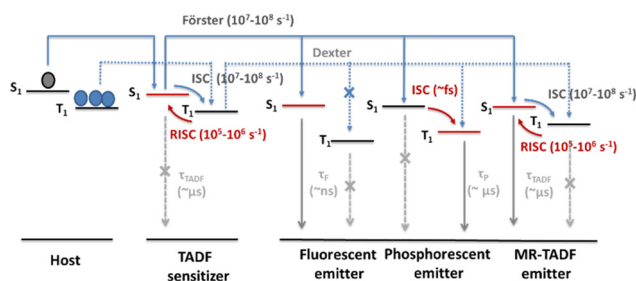


Fig. 3 Diagram of the energy transfer process of the TADF-sensitized system.

the RISC process in the exciplex sensitizer. The singlet excitons can be harvested through the FET of singlets between the exciplex and the emitter. Both exciplexes and TADF sensitizers focus on fast up-conversion processes. However, the up-conversion efficiency of exciplexes is lower than that of TADF materials. The exciplex can also be the co-host of the sensitized systems, whether TADF-sensitized or phosphorescence-sensitized. The exciplex:sensitizer:emitter system has an additional RISC process compared to the host:sensitizer:emitter system, facilitating the FET while suppressing the DET and avoiding charge recombination on the emitter.

In conclusion, some commonalities in the mechanisms of the sensitized OLEDs with different sensitizers can be found as follows: (i) the absorption spectrum of the emitter should have a suitable spectral overlap with the PL spectrum of the sensitizer to ensure the efficiency of the FET, (ii) the HOMO/LUMO levels between the sensitizer and the emitter should be matched or the doping concentration of the emitter should be reduced to avoid direct exciton formation by charge trapping on the emitter, and (iii) good thermal and morphological stability is necessary to extend the device lifetime. Equally important, the difference between the sensitizer and the emitter leads to a different characterization of the energy transfer process: (i) the DET process has different magnitudes of influence on the efficiency of the sensitized OLEDs due to the consideration of triplet excitons, (ii) the exciton transfer paths are different in different sensitized systems, and (iii) the rate-determining steps in the energy transfer process are different. In a phosphorescence-sensitized system, the slow  $k_{FET}$  limits the utilization of triplet excitons. In a TADF/exciplex-sensitized device, the  $k_{RISC}$  impedes high-efficiency energy transfer.

## Phosphorescence-sensitized OLEDs

In phosphorescence-sensitized OLEDs, the role of the phosphorescent sensitizer is to use the spin–orbit coupling effect caused by heavy metal atoms to effectively convert  $S_1$  to  $T_1$  excitons and then transfer the excitons to the emitter through the FET energy transfer process. It is possible to reduce triplet exciton density and shorten the lifetime of triplet excitons.

### Phosphorescence-sensitized fluorescent OLEDs

As mentioned above, the low EQE is the main bottleneck for developing FOLEDs. Introducing the phosphorescent sensitizer is one of the most effective ways to increase the EQE of FOLEDs. The phosphorescence-sensitized fluorescent device performances are shown in Table 1. The chemical structures of sensitizers and emitters are shown in Fig. 4.

In blue phosphorescence-sensitized fluorescent (PSF) OLEDs, the efficient phosphorescent sensitizer should emit light in the absorption spectrum of the emitter to ensure sufficient energy transfer. However, the design difficulties of deep-blue phosphorescent materials limit the development of blue PSF OLEDs. Besides, high exciton energy typically results in device instability. Several recent studies have addressed

Table 1 Summarized device performances of the phosphorescence-sensitized fluorescent OLEDs

Host	Phosphorescent sensitizer	Fluorescent emitter	EQE <sub>max/1000</sub> <sup>a</sup> (%)	PE <sub>max/1000</sub> <sup>b</sup> (lm W <sup>-1</sup> )	CE <sub>max/1000</sub> <sup>c</sup> (Cd A <sup>-1</sup> )	Ref.
mCBP: TSP01	(dfpysipy) <sub>2</sub> Ir(mpic)	TBPe	15.3/5.6	15.7/2.4	18.0/7.7	26
28CzDBF	Ir(cb) <sub>3</sub>	TBPDP	11.6/—	—/—	—/—	22
TCTA: B4PyMPM	Ir(ppy) <sub>2</sub> tmd	DCJTB	23.7/—	—/—	—/—	28
TCTA: B4PYMPM	Ir(ppy) <sub>3</sub>	TBRb	25.0/24.8	100.4/82.2	—/—	29
TCTA: B4PYMPM	Ir(ppy) <sub>2</sub> tmd	TBRb	26.1/26.0	114.3/91.9	—/—	
DIC-TRZ	Ir(mppy) <sub>3</sub>	C545T	25.1/24.4	95.0/—	84.8/82.6	30
PCTF	Ir(ppy) <sub>2</sub> acac	TBRb	24.2/—	50.2/—	—/—	31

<sup>a</sup> EQE<sub>max/1000</sub> – the maximum EQE and EQEs at 1000 cd m<sup>-2</sup>. <sup>b</sup> PE<sub>max/1000</sub> – the maximum power efficiency and PEs at 1000 cd m<sup>-2</sup>. <sup>c</sup> CE<sub>max/1000</sub> – the maximum current efficiency and CEs at 1000 cd m<sup>-2</sup>.

these obstacles. Kim *et al.* reported a highly efficient blue OLED constructed with a phosphorescent sensitizer and a conventional fluorescent emitter (TBPe).<sup>28</sup> Even though the wavelength difference between the phosphorescence and fluorescence emissions was only 10 nm, the fluorescent dopant still predominated the emission. The EQE of the sensitized device was 15.3%, which is 2.2 times that of the non-sensitized device (7%).

Also, Robert Lovrincic *et al.* cleverly proposed a dual-emitting system based on the unicolor phosphorescence-sensitized fluorescence (UPSF) to achieve stable blue OLEDs.<sup>24,29</sup> The sensitizer in the UPSF system has a similar emission spectrum to that of the emitter. The sky-blue emission color of the sensitizer was maintained by modulating the emission of the sensitizer and the emitter in the UPSF OLEDs. The EQE of

the device at 1000 cd m<sup>-2</sup> was 11.6%. In addition, to better comprehend the potential of the UPSF system, a multiscale model of the UPSF OLED was developed to demonstrate that neither the PLQY nor the radiation decay time can be improved by adding more acceptors. Further examination of the ideal UPSF system revealed that the suppression of Dexter transfer could result in high efficiency and a long lifetime. These studies demonstrate that when phosphorescent materials are used as sensitizers for blue fluorescent materials, it is possible to match the emission of the phosphorescent material with that of the fluorescent material and to adjust the FET and DET processes to design a suitable sensitized device without having to design a UV-emitting phosphorescent sensitizer, which significantly simplifies material design.

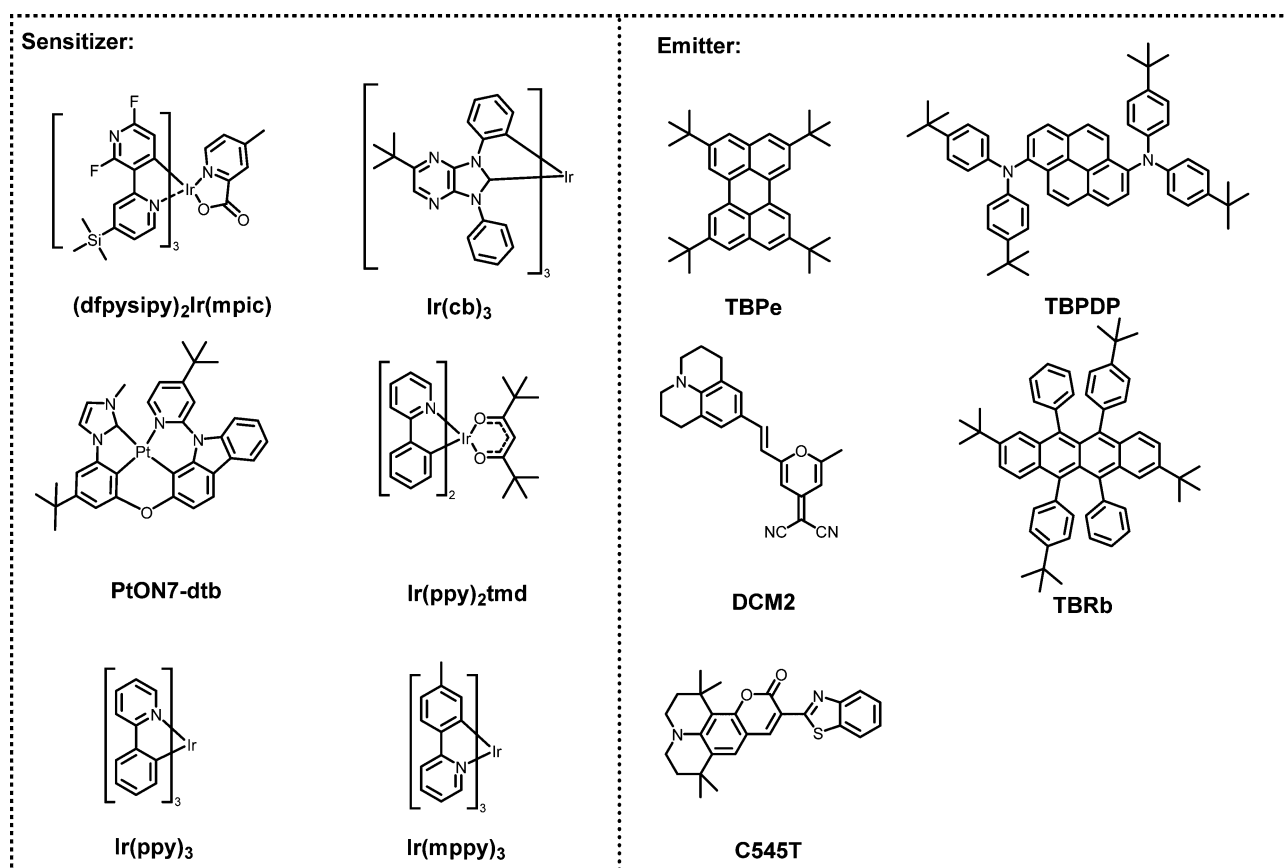


Fig. 4 Chemical structures of phosphorescent sensitizers and fluorescent emitters.

Increasing the additional exciton transfer pathway, also known as the multiple-sensitized process, is one method for further efficiency enhancement. Using a host with TADF properties in conjunction with phosphorescent materials to co-sensitize the dopant increases the additional transfer pathway of excitons. The maximum efficiency of PSF OLEDs with different emission wavelengths has been attained through a multiple-sensitized process.

In the red PSF OLEDs, Kim *et al.* reported a FOLED using an iridium (Ir) complex as a sensitizer in an exciplex co-host system.<sup>30</sup> In contrast to conventional FOLEDs based on an exciplex co-host, when the Ir complex was co-doped, not only the triplet excitons can be converted into singlet excitons, but they can also be transferred to a triplet phosphorescent sensitizer. As a result, the singlet portion of the excitons in the fluorescent dopant increases. The FET process and sensitizer radiation decay rates were estimated and discovered that more than 80% of excitons were transferred to DCJDCB. The EQE of the device increased from 10.6% to 23.7%. This method had also been utilized in the development of yellow FOLEDs.<sup>31</sup> Due to the high PLQY, the EQE of devices employing Ir(ppy)<sub>3</sub> and Ir(ppy)<sub>2</sub>tmd as sensitizers reached 26.1% and 25%, respectively. The EQE of these works was the highest for the yellow and red PSF OLEDs.

Using DIC-TRZ as the TADF host, Ir(mppy)<sub>3</sub> as the phosphorescent sensitizer, and C545T as the emitter, Wang *et al.* manufactured efficient green PSF OLEDs in 2021.<sup>32</sup> The results demonstrated that the sensitized system, in conjunction with the TADF host and the phosphorescent sensitizer, was conducive to triplet excitons, thereby increasing the efficiency. Moreover, the increased HOMO energy inhibited the direct carrier capture of the dopant. The optimal C545T-based device achieved an EQE of 25.1%.

Recently, Duan *et al.* adopted this ternary system and dubbed this concept phosphor-assisted TADF-sensitized fluorescence.<sup>33</sup> Unlike the widespread research into TADF materials in pursuit of a high RISC process, this work suggested that the ISC process also played a significant role in the energy transfer process, competing with the FET and influencing exciton utilization. Due to the unidirectional sensitization from phosphorescence (Ir(ppy)<sub>2</sub>acac) to fluorescence (TBRb) and the host of anti-aggregation-caused quenching characteristics (PCTF), the photoluminescence decay curve of TPSF had a nanosecond lifetime

and no noticeable long delay tail. The maximum EQE of 24.2% was achieved for PSF OLEDs based on the TBRb emitter. Unbelievably, the device also exhibited a very low-efficiency roll-off, with an L<sub>90</sub> (the luminance at which EQE falls to 90% of its maximum value) exceeding 190 500 cd m<sup>-2</sup>.

### Phosphorescence-sensitized MR-TADF OLEDs

Despite the bottleneck increase in the EQE achieved by PSF OLEDs, the broadband emission and large Stokes shift of the fluorescent emitter limit their application in the sensitized OLED. Hatakeyama *et al.* published the MR-TADF materials in 2016 by designing planar aromatic compounds containing boron and nitrogen.<sup>9</sup> MR-TADF materials, with a high PLQY, narrowband emission, and small Stokes shift, are currently the most suitable emitters for high color purity sensitized OLEDs.<sup>34</sup> The phosphorescence-sensitized MR-TADF device performances are shown in Table 2. The chemical structures of sensitizers and emitters are shown in Fig. 5.

In 2019, Lee *et al.* first synthesized *t*-DABNA with *tert*-butyl groups around the resonance core structures of B and N to avoid strong intermolecular interactions.<sup>35</sup> The deep-blue TADF device emitted at 464 nm with a full width at half maximum (FWHM) of 27 nm achieved a maximum EQE of 22.8%. Due to the long-delayed fluorescence lifetime, the *t*-DABNA device suffered a significant efficiency roll-off. The group thus constructed deep-blue phosphorescence-sensitized MR-TADF OLEDs.<sup>36</sup> Several blue phosphorescent materials were evaluated as potential sensitizers. Ir(cb)<sub>3</sub> was the most favorable since its PL spectrum overlaps mostly with *t*-DABNA's absorption. The corresponding sensitized device achieved an EQE of 24.8% with the CIE coordinates (0.131, 0.107). The LT<sub>50</sub> (time to 50% of the initial luminance) of the device was 293 h at 200 cd m<sup>-2</sup>, 17 times greater than the device without the sensitizer.

To further increase the EQE, Chi *et al.* designed a series of Ir compounds to sensitize *t*-DABNA in 2021.<sup>37,38</sup> They proposed a series of homogeneous Ir(III) complexes with three 2-phenyl-1,2,4-triazole-3-ylidene cyclometalates. The deep-blue-emitting Ir(III) complexes (*m*-tz1 and *m*-tz2) were suitable candidates to sensitize the emitter as their emission peaks were located at 400 and 420 nm, respectively. Sensitized devices based on *t*-DABNA exhibited high EQE values of 16.7% and 19.7%, respectively, which were higher than devices without the sensitizer

Table 2 Summarized device performances of the phosphorescence-sensitized MR-TADF OLEDs

Host	Phosphorescent sensitizer	Fluorescent emitter	EQE <sub>max/1000</sub> <sup>a</sup> (%)	PE <sub>max/1000</sub> <sup>b</sup> (lm W <sup>-1</sup> )	CE <sub>max/1000</sub> <sup>c</sup> (Cd A <sup>-1</sup> )	Ref.
mCBP	Ir(cb) <sub>3</sub>	<i>t</i> -DABNA	24.8/18.4	20.2/8.5	22.6/16.7	36
DPEPO	<i>m</i> -tz1	<i>t</i> -DABNA	16.7/—	14.8/—	20.0/—	37
DPEPO	<i>m</i> -tz2	<i>t</i> -DABNA	19.7/—	17.5/—	20.0/—	
mCBP	<i>f</i> tpb1	<i>t</i> -DABNA	29.6/—	28.7/—	19.6/—	38
SiCzCz: SiTrzCz2	PtON-TBBI	<i>t</i> -DABNA	23.7/—	—/—	26.2/—	39
SiCzCz: SiTrzCz2	PtON-TBBI	TBE01	25.4/—	—/—	27.1/—	
SiCzCz: SiTrzCz2	PtON-TBBI	TBE02	25.8/—	—/—	27.0/—	
mCBP: SiCz2Trz	CN-Ir	<i>ν</i> -DABNA	27.3/23.3	—/—	27.7/—	40
oCBP: mCBP-4CN	PtON7-dtb	<i>ν</i> -DABNA	32.2/25.4	—/—	32.0/25.1	41

<sup>a</sup> EQE<sub>max/1000</sub> – the maximum EQE and EQEs at 1000 cd m<sup>-2</sup>. <sup>b</sup> PE<sub>max/1000</sub> – the maximum power efficiency and PEs at 1000 cd m<sup>-2</sup>. <sup>c</sup> CE<sub>max/1000</sub> – the maximum current efficiency and CEs at 1000 cd m<sup>-2</sup>.

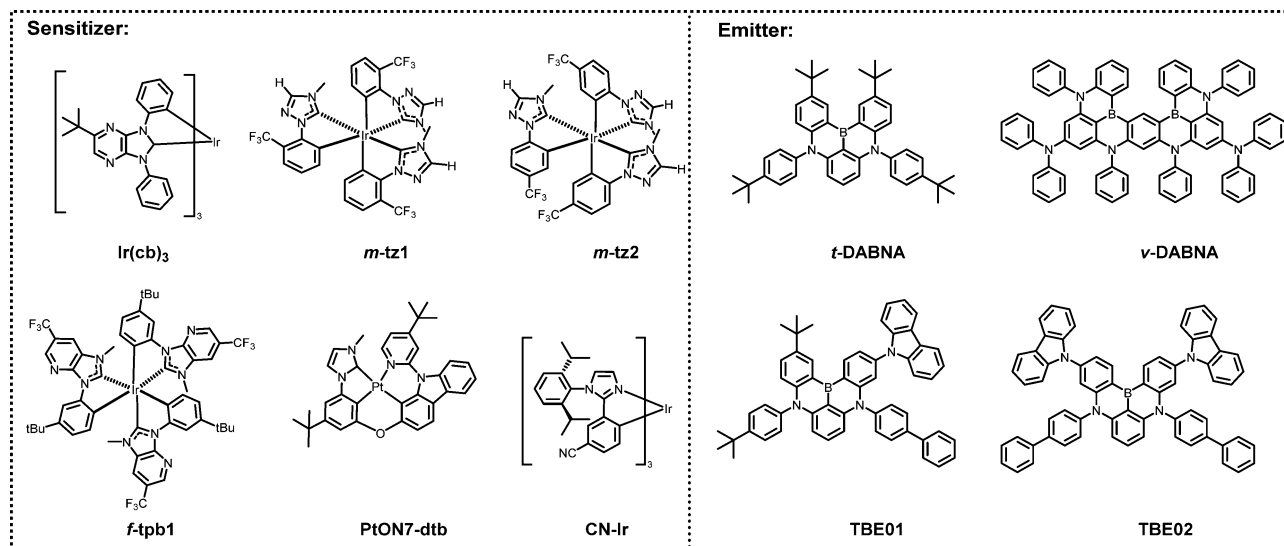


Fig. 5 Chemical structures of phosphorescent sensitizers and MR-TADF emitters.

(14.8% for DPEPO: *t*-DABNA). Nonetheless, the EQE was not prominent in the sensitized device employing *t*-DABNA as the TADF terminal emitter due to the poor emission efficiency of the sensitizer and the unsuitable device structure. By increasing the  $\pi$ -conjugation of carbinol chelates, the group has recently synthesized multiple similar molecules (*m*-tpb1, *m*-tpb2, *f*-tpb1, and *f*-tpb2). These molecules exhibited superior photophysical properties compared to *m*-tz1 and *m*-tz2. The device employing *f*-tpb1 as a sensitizer achieved an exceptional EQE of 29.6%, the most remarkable performance of *t*-DABNA-based sensitized devices in recent years. It is a pity that neither of these articles mentions the relevant device's lifetime. A comparison of the two sensitized devices shows that a large PLQY value is a critical element in improving efficiency.

The sensitized *t*-DABNA devices achieved improvement in the EQE, but they still had a lifetime shortcoming. Chu *et al.* designed two new MR-TADF materials, TBE01, and TBE02, by adding a carbazole group to the periphery of *t*-DABNA.<sup>39</sup> The materials exhibited a high molar extinction coefficient, a fast RISC rate, and weak hole-trapping characteristics. PtON-TBBI exhibiting suitable photocharacteristics and excellent stability was used as a phosphorescent sensitizer. SiCzCz:SiTrzCz2 showing a low  $\Delta E_{ST}$  and a short exciton lifetime was selected as the host. In addition, the high molar extinction coefficient of MR-TADF also contributes to the FET process. The corresponding devices exhibited high EQEs of 25.4% and 25.8%, respectively. More importantly, the device's lifetime was improved by 6.6 times compared to the previously reported device. The top-emitting device shows state-of-the-art device performances with a lifetime of 681 h at 1260 cd m<sup>-2</sup>, a CCE of 441 cd A<sup>-1</sup> CIE<sub>y</sub><sup>-1</sup> and a CIE<sub>y</sub> value of 0.058.

*v*-DABNA was a molecule synthesized by Hatakeyama *et al.* in 2019 based on the DABNA molecule.<sup>11</sup> The electroluminescence spectra of *v*-DABNA devices demonstrated deep blue emission with a peak maximum of 469 nm, an FWHM of 18 nm, and an EQE as high as 34.4%. Due to the small FWHM, the color

coordinate of the device was (0.12, 0.11). However, the devices also experienced a severe efficiency roll-off. By doping the sensitizer, the sensitized *v*-DABNA devices also achieved high efficiency, narrow-band emission, and low roll-off. In addition, the EQE and lifetime of the sensitized *v*-DABNA devices were more remarkable than those of the *t*-DABNA-based devices.

In 2021, Lee *et al.* created energy exchange phosphorescent and TADF (EPHTADF) devices.<sup>40</sup> The key to the EPHTADF mechanism is the simultaneous forward and backward energy transfer between the phosphorescence sensitizer and the TADF emitter. The extra pathways to the singlet of the TADF are created by giving the phosphorescent sensitizer the same triplet energy as the emitter's singlet energy. The process reduces the triplet exciton lifetime in the emitter. CN-Ir, showing a short phosphorescence lifetime, high EQE, and device stability, was selected as a sensitizer for *v*-DABNA. The EQE of the EPHTADF device was 27.3%. The LT<sub>50</sub> of the EPHTADF-OLED was 121 h (1000 cd m<sup>-2</sup>), over five times longer than the device without a sensitizer. To further improve the purity and efficiency, a top-emitting device with a maximum CE value of 37.0 cd A<sup>-1</sup> was developed. The LT<sub>50</sub> of the top-emitting device was increased to 493 h at 1000 cd m<sup>-2</sup>, which can be converted to 31 130 h at 100 cd m<sup>-2</sup>.

In addition to Ir complex sensitizers, Pt complexes have also shown superior performance as sensitizers. The PtON7-dtb molecules were used as sensitizers for *v*-DABNA by Hyeonho Choi *et al.*<sup>41</sup> The OLED device achieved a maximum EQE as high as 32.2%, which was due to the high PLQY and outcoupling efficiency. This device also exhibited the LT<sub>50</sub> of 156.3 h at a luminance of 1000 cd m<sup>-2</sup>. The group had also prepared a top emitting device. Compared to the bottom-emitting device, the top-emitting device exhibited a narrower FWHM, and the lifetime was increased to 253.8 h. The lifetimes of the devices are one of the highest values reported for the blue-sensitized OLEDs.

As described above, the introduction of phosphorescent sensitizers effectively improves the efficiency of fluorescent



and MR-TADF OLEDs, while extending the lifetime of MR-TADF OLEDs. Phosphorescent sensitizers with high PLQY values are key for improving the EQE of sensitized OLEDs. Additionally, the large spectral overlap between the phosphorescent sensitizer and emitter can effectively facilitate FET energy transfer and thus increase EQE. However, the lack of efficient deep-blue phosphorescent materials has hindered the development of sensitized devices.

## TADF-sensitized OLEDs

Owing to the efficient triplet exciton availability, the TADF material is also one of the good candidates for sensitizers. When TADF materials are used as a sensitizer, the triplet excitons on the TADF sensitizer are upconverted to singlet excitons by the RISC process. Then, the singlet exciton is resonantly transferred to the emitter molecules through a FET process, thereby increasing the exciton utilization of the device. As the TADF sensitizer only takes on the function of the exciton transfer in the machine, the problem of color purity caused by the direct luminescence of the TADF material is subtly resolved. In addition, due to the limitations of blue phosphorescent materials, the TADF-sensitized OLEDs show more efficient performance than the phosphorescence-sensitized OLEDs.

### TADF-sensitized fluorescent OLEDs

The sensitized devices using TADF materials as sensitizers and fluorescence as emitters originated in 2014. Adachi *et al.* prepared the sensitized devices *via* a cascade energy transfer scheme in which the yellow, green, red, and blue TADF molecules with the small  $\Delta E_{ST}$  Tri-PXZ-TRZ, PXZ-TRZ, ACRXTN, and ACRSA were used as sensitizers to ensure a fast RISC process.<sup>14</sup> The corresponding fluorescent molecules DBP, TBRb, TTPA, and TBPe were selected as emitters to match them. The absorption spectra of all sensitizers and the emission spectra of the emitters overlapped. The maximum EQE of devices based on these materials reached 13.4–18%. The sensitized devices are also known as HF technology, which can achieve up to four times the fluorescence intensity of the conventional fluorescent emitter while solving the wide spectrum problem of the TADF materials. Almost at the same time, to solve the problem that the small  $\Delta E_{ST}$  contradicts the large radiative decay rate in TADF materials, Duan *et al.* introduced materials with the small  $\Delta E_{ST}$  as sensitized hosts (DIC-TRZ and PIC-TRZ) for the yellow fluorescent dopant (DDAF), which was referred as the TSF mechanism.<sup>15</sup> The EQE of the yellow FOLEDs reached 11.7% and 4.5%, respectively. These two studies combine high-purity and high-PLQY fluorescent emitters with TADF materials that have high exciton utilization, breaking through the 5% theoretical limit of traditional FOLED performance and providing guidance for the theory of the TSF devices. Since then, several research studies on devices based on fluorescent materials as emitters have focused on designing high EQE TSF OLEDs.

In the TSF OLEDs, the fast RISC process from the triplet to the singlet is crucial for efficiently utilizing triplet excitons for TADF sensitizers. Cui *et al.* designed and synthesized a TADF

material, 5Cz-TRZ, consisting of multiple carbazole donors and one triazine acceptor.<sup>42</sup> Due to the strong spin-orbit coupling between the local-excitation-dominated  $T_1$  state and the charge transfer-dominated  $S_1$  state and a dense manifold of triplet states resulting from the formation of charge-resonance-type hybrid triplet states, 5Cz-TRZ showed an extremely fast  $k_{RISC}$  of  $1.5 \times 10^7 \text{ s}^{-1}$ . The EQE of TSF OLEDs employing this material to sensitize TBPe, TMDQA, TBRb, and DCJTb reached 24%, 22.3%, 24.9%, and 23.5%, respectively. The slightly lower EQE compared to the 5Cz-TRZ-only device (29.6%) was attributed to the shallower HOMO level of its fluorescent material compared to that of 5Cz-TRZ. In the blue TSF OLEDs, DMAC-DPS, a blue TADF material, was used as a sensitizer.<sup>43</sup> The vertical alignment of the donor and the acceptor effectively suppressed the molecular packing and triplet exciton annihilation, even in the case of high doping. The device with DMAC-DPS as a sensitizer and TBPe as an emitter achieves a high EQE of 18.5%. CzAcSF, which replaces one acridine unit of DMAC-DPS with a weak electron-donating carbazole, was also used as a sensitizer.<sup>44</sup> Benefiting from the PLQY and high doping ratio (CzAcSF:TBPe = 50:0.1), the TSF device based on TBPe as the emitter achieved a high EQE of 18.1%. Interestingly, the device used a single host system. The TADF-sensitized fluorescent device performances are shown in Table 3. The chemical structures of sensitizers and emitters are shown in Fig. 6.

In addition to the efficient TADF sensitizer, energy transfer between the sensitizer and the emitter is also crucial in the sensitized system. Lee *et al.* constructed the multilayer luminescent layer structure by spatially separating the TADF sensitizer DMAC-DPS from the TBPe fluorescent molecule.<sup>45</sup> The device with alternating DPEPO:DMAC-DPS and DPEPO:TBPe layers realized a maximum EQE of 18.8%, which was attributed to the suppression of the DET process by the separation of DMAC-DPS and TBPe fluorescent molecules.

A green TADF material with a high PLQY and a small  $\Delta E_{ST}$  of 25.9 meV, DACT-II, was also selected for the sensitizer of the PhtBuPAD fluorescent molecules in the green TSF OLED.<sup>46</sup> Four types of TSF OLEDs were designed based on these molecules by Duan *et al.* by considering the host type (TADF or non-TADF) and the carrier recombination position (on the host or the TADF sensitizer). The excitons on the host reduced the  $T_1$  exciton density on the TADF sensitizer while increasing the  $S_1$  exciton ratio and improving exciton utilization compared to recombination on the TADF sensitizer. When the TADF materials are used as the host, the multiple sensitized processes greatly enhance the FET rate while suppressing the DET rate. The results indicated that the EQE of the device based on the TADF host and the carrier form on the host reached a maximum value of 23.2%, with a power efficiency (PE) value of  $76.9 \text{ lm W}^{-1}$ .

DACT-II was also used as a sensitizer for the yellow emitter (TBRb).<sup>47</sup> You *et al.* designed and synthesized TADF molecules using a methyl-shielding strategy, 8-MeACRXTO, 1-MeACRXTO, and d-MeACRXTO, in which the xanthone (XTO) backbone was used as the electron acceptor and 9,9-dimethyl-9,10-dihydroacridine (ACR) as the donor. The device based on MeACRXTO as the host,



Table 3 Summarized device performances of the TADF-sensitized fluorescent OLEDs

Host	TADF sensitizer	Fluorescent emitter	EQE <sub>max/1000</sub> <sup>a</sup> (%)	PE <sub>max/1000</sub> <sup>b</sup> (lm W <sup>-1</sup> )	CE <sub>max/1000</sub> <sup>c</sup> (Cd A <sup>-1</sup> )	Ref.
DPEPO	ACRSA	TBPe	13.4/8.7	18.0/7.0	27.0/18.0	14
mCP	ACRXTN	TTPA	15.8/11.7	47.0/30.0	45.0/38.0	
mCBP	PXZ-TRX	TBRb	18/17.2	58.0/33.0	60.0/56.0	
CBP	tri-PXZ-TRZ	DBP	17.5/10.9	28.0/10.0	25.0/20.0	
—	DIC-TRZ	DDAF	11.7/5.5	44.1/14.3	36.4/17.1	15
—	PIC-TRZ	DDAF	4.5/3.9	12.3/7.5	12.7/11.2	
mCBP	5Cz-TRZ	TBPe	24.0/—	—/—	—/—	42
mCBP	5Cz-TRZ	TMDQA	22.3/—	—/—	—/—	
mCBP	5Cz-TRZ	TBRb	24.9/—	—/—	—/—	
mCBP	5Cz-TRZ	DCJTB	23.5/—	—/—	—/—	
DPEPO	CzAcSF	TBPe	18.1/—	31.2/—	29.8/—	44
DPEPO	DMAC-DPS	TBPe	18.8/13.5	34.4/12.4	—/—	45
m32aICT	DACT-II	PhtBuPAD	23.2/—	76.9/—	—/—	46
ACRXTO	DACT-II	TBRb	19.6/14.2	79.0/28.7	—/—	47
8-MeACRXTO	DACT-II	TBRb	25.5/18.6	109.0/44.4	—/—	
1-MeACRXTO	DACT-II	TBRb	19.5/16.9	75.2/36.0	—/—	
dMeACRXTO	DACT-II	TBRb	32.3/23.5	118.2/49.0	—/—	
32alCTRZ	DACz-TAZTRZ	TBRb	23.7/23.2	82.1/58.1	—/—	48
B3PYMPM	TPA-DCPP	BPPC	5.4/—	—/—	—/—	49
CBP	TPAB-BF2	BPPC-Ph	3.8/—	—/—	—/—	50
mCBP	TPA-PZTCN	BBT-TPA	1.1/—	—/—	—/—	51
SFBCz: SFTRZ	5TCzBN	TBRb	21.7/21.4	78.0/69.6	—/—	52

<sup>a</sup> EQE<sub>max/1000</sub> – the maximum EQE and EQEs at 1000 cd m<sup>-2</sup>. <sup>b</sup> PE<sub>max/1000</sub> – the maximum power efficiency and PEs at 1000 cd m<sup>-2</sup>. <sup>c</sup> CE<sub>max/1000</sub> – the maximum current efficiency and CEs at 1000 cd m<sup>-2</sup>.

and DACT-II as the sensitizer, achieved a record-high EQE of 32.3%, the highest reported for the TSF-OLEDs.

In the yellow TSF OLED, a new triazolotriazine (TAZTRZ) acceptor was designed to combine with the 3,6-(diphenylamine)carbazole (DACz) donor to form the TADF material.<sup>48</sup> TAZTRZ has a strong electron-withdrawing ability, leading to a well-separated distribution of FMOs, thus reducing  $\Delta E_{ST}$  and accelerating the RISC process. Based on DACz-TAZTRZ, a turn-on voltage of 2.1 V, a high EQE of 23.7%, and a PE of 82.1 lm W<sup>-1</sup> are achieved. The device has one of the most advanced device performances currently available for the yellow FOLEDs.

Sensitizers are also deployed in near-infrared (NIR) OLEDs to improve the device's efficiency. In 2019, Cohen *et al.* prepared highly efficient NIR OLEDs using TPA-DCPP as a sensitizer.<sup>49</sup> BPPC was selected as an emitter owing to easily tuned emission and high PLQY values. The sensitized NIR OLED achieved a maximum EQE of 5.4%, with an electroluminescence maximum at 790 nm. Subsequently, the group used an efficient TADF boron difluoride curcuminoid derivative (BF2) as a strong electron acceptor to attain deep-NIR wavelengths.<sup>50</sup> To further red-shift the NIR wavelengths, a TADF sensitized system was employed. The sensitized NIR OLED emitting at 790 nm showed an EQE of up to 3.8%, with a FWHM < 40 nm. In addition, transport measurements demonstrated that holes are formed on the host and then transferred to the sensitizer to form electrons with electrons.

The same year, Adachi *et al.* also reported a donor-acceptor type sensitizer, TPA-PZTCN, for the deep-NIR-fluorophore.<sup>51</sup> TPA-PZTCN had a high  $k_{RISC}$  benefiting from a small  $\Delta E_{ST}$  and the energetically closed T<sub>2</sub> state. BBT-TPA, with relatively high PLQYs but no TADF characteristics, was used as the emitter. The films doped with TPA-PZTCN and BBT-TPA had higher PLQY values than that of BBT-TPA. The sensitized OLED

achieved a maximum EQE of 1.1% with a peak wavelength of 901 nm.

Exciplexes as the host of TSF OLEDs also help achieving a highly efficient and long lifetime. In 2020, Duan *et al.* utilized the bulky spirofluorene unit as a  $\pi$ -spacer to expand the distance between the electron donor and the electron acceptor subunits of  $\pi$ -donor and  $\pi$ -acceptor molecules to construct the sky-blue exciplex (SFBCz:FTRZ) with high T<sub>1</sub> energies and fast RISC rates.<sup>52</sup> 5TCzBN with high stability was selected as the sensitizer, and the surrounding *tert*-butyl units can eliminate the DET process. The white devices based on exciplex:5TCzBN:TBRb as the light-emitting layer recorded a high EQE of 21.7% and a record-high maximum PE of 78 lm W<sup>-1</sup>. The device exhibits excellent stability (a T<sub>80</sub> > 8200 h at 1000 cd m<sup>-2</sup>).

### TADF-sensitized phosphorescent OLEDs

TADF materials can be used not only as sensitizers for fluorescent materials but also for phosphorescent materials. Phosphorescent materials use the spin-orbit coupling effect caused by the heavy atom effect to allow T<sub>1</sub> excitons to decay radiatively and thus emit light. However, the triplet exciton lifetime of phosphorescent materials is generally in the microsecond range, which leads to PhOLEDs with serious efficiency roll-off at high current densities. In addition, high manufacturing costs due to the need for precious metals remain a problem for PhOLEDs. The TADF-sensitized phosphorescent device performances are shown in Table 4. The chemical structures of sensitizers and emitters are shown in Fig. 7.

To address the problems of traditional PhOLEDs, Duan *et al.* proposed the TSP mechanism by combining TADF hosts with phosphorescent emitters. PIC-TRZ that exhibited a small  $\Delta E_{ST}$  of 0.11 eV was selected as the sensitizer and Ir(ppy)<sub>3</sub> as the phosphorescent emitter.<sup>17</sup> The maximum CE of the TSP OLED

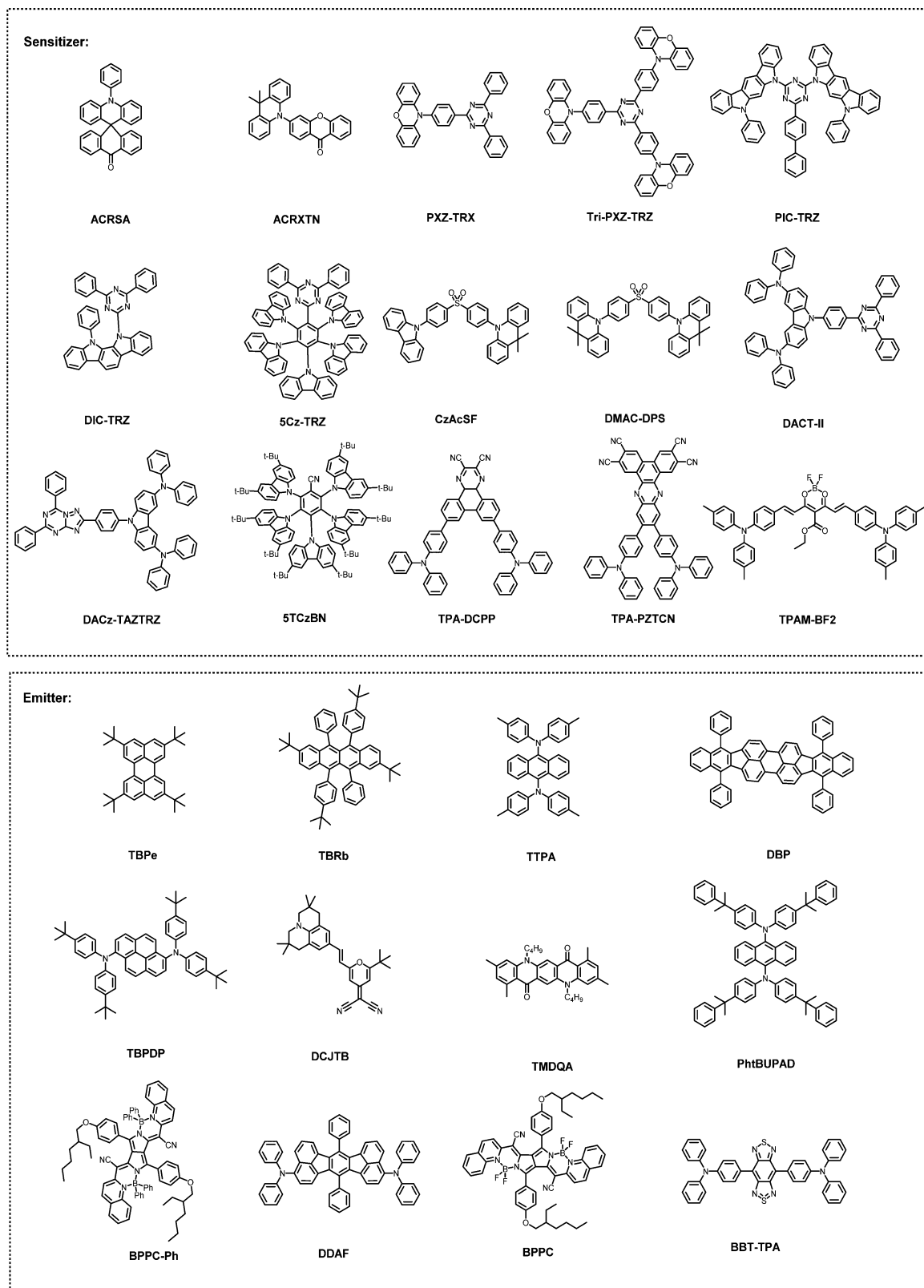


Fig. 6 Chemical structures of TADF sensitizers and fluorescent emitters.

was  $68 \text{ cd A}^{-1}$ , and the roll-off was significantly suppressed (the CE of  $62 \text{ cd A}^{-1}$  at  $10\,000 \text{ cd m}^{-2}$ ) due to its more balanced bipolar characteristics. Subsequently, they designed and

synthesized four TADF materials based on PIC-TRZ (POBICT, BICT, PBICT, and BICT).<sup>53</sup> The  $\Delta E_{\text{ST}}$  of these TADF materials decreases sequentially. PO-01 was selected as the

phosphorescent emitter. Among the devices using these materials as the host, the orange TSP OLED based on PBICT as the host exhibited a maximum EQE of 24.5%, a maximum PE of 64.5%, a low drive voltage of 2.75 V, and an extremely small efficiency roll-off (the EQE of 23.8% at 10 000  $\text{cd m}^{-2}$ ). Although BBICT has the smallest  $\Delta E_{\text{ST}}$ , the carrier trapping is reduced due to the lower LUMO level. The device lifetimes of 955 and 1910 h were achieved in PBICT and BBICT-based devices, respectively. In these studies, it was shown that fine-tuning the  $\Delta E_{\text{ST}}$  of the TADF sensitizer helps reduce the voltage and improve the device performance when the energy levels of the devices are matched.

Another function of the TADF sensitizer is to reduce the cost, which can be attributed to the fact that using hosts with TADF promotes energy transfer, resulting in a lower concentration of the dopant required for the system. Duan *et al.* chose PBICT as the host for green phosphor, Ir(ppy)<sub>3</sub>.<sup>54</sup> The maximum EQE of the PBICT-based device is 23.9% at a low dopant concentration of 3 wt%. In contrast, for devices with CBP as the host, a similar EQE value is achieved with the dopant concentration in the range of 5–8 wt%. In addition, the device achieves a longer lifetime at low doping concentrations. Liao *et al.* showed the excellent device performance at much lower concentrations.<sup>55</sup> TADF-type hosts (OSTFPCN and OSTFPB) were synthesized based on oxygenated spiro-triphenylamino-fluorenyl-triphenylamine (OSTF) and cyano- and bis-(2,4,6-trimethylphenyl) borane, which has a small  $\Delta E_{\text{ST}}$ , balanced carrier transporting ability and effective ET ability. The device with Ir(MDQ)<sub>2</sub>(acac) as the emitter achieved 63.6  $\text{lm W}^{-1}$  of PE and 31.2% of EQE at a low phosphorescent doping concentration (0.5 wt%). The underlying cause of the optimum performance of OLEDs with low phosphorescent concentrations is that the up-conversion process of the TADF material allows the devices to be expected to complete the energy transfer at lower dopant concentrations.

Fan *et al.* designed and synthesized a TADF material, namely Trz-PhCz, with a small  $\Delta E_{\text{ST}}$  by combining the donor (carbazole) and acceptor (triazine) and used it as the sensitizer of the blue, green, yellow, orange, and red phosphorescent emitter

based on Firpic, Ir(ppy)<sub>2</sub>(acac), PO-01, Ir(dmppm)<sub>2</sub>(acac), and Ir-F-DHBA.<sup>56</sup> Trz-PhCz exhibits a short triplet lifetime. The orange device based on Ir(dmppm)<sub>2</sub>(acac) as the emitter achieves a record-high EQE of 31.4%, while the yellow and red devices also achieved high EQEs of 27.3% and 30.4%. In particular, the green device with a maximum PE of 111.8  $\text{lm W}^{-1}$  and a maximum EQE of 24.3% was developed. Notably, the device also shows an extremely low-efficiency roll-off. At a brightness of 10 000  $\text{cd m}^{-2}$ , the EQE is maintained at 20.6%, with an EQE drop of merely 15.2%, which is attributed to the small dipole moment and a short triplet lifetime. The WOLED devices were prepared based on Trz-PhCz:Firpic:PO-01 as the light-emitting layer, with a maximum EQE of 26.5% and a maximum PE of 102.5  $\text{lm W}^{-1}$ .

In TADF-sensitized phosphorescent systems, the short-range DET process between the TADF sensitizer and the emitter plays an important role. Yang *et al.* used DMAC-DPS and a similar molecule, 4CzDMAC-DPS, as the TADF sensitizer, where 4CzDMAC-DPS was surrounded by carbazole substituents to regulate the intermolecular distance.<sup>57</sup> The iridium dendrimer R-D2 with the core tris(2-thienyl-4-phenyl) iridium [Ir(Th-PQ)<sub>3</sub>] was selected as the emitter. A higher energy transfer efficiency from DMAC-DPS to R-D2 was found by estimating the ratio of the PL intensity from the emission peak. The red device based on DMAC-DPS as the TADF sensitizer achieved a maximum EQE of 22.2%, which is higher than that of the 4CzDMAC-DPS-based device (EQE = 15.6%). This EQE is one of the highest values for the solution-processed red PhOLEDs. Due to the larger distance and the faster RISC rate, the 4CzDMAC-DPS-based device exhibits a rather low-efficiency roll-off of 9.0% at 1000  $\text{cd m}^{-2}$ . As a result, the TADF sensitizer with the additional hindrance units has a lower efficiency roll-off in the TSP OLED, while TADF hosts without any peripherals facilitate the DET and FET processes, thus achieving high efficiency.

The accumulation of large numbers of excitons in the triplet state of phosphorescent materials is one of the factors leading to the energy loss of excitons and device performance. Liao *et al.* used exciplex and TADF materials as the host and

**Table 4** Summarized device performances of the TADF-sensitized phosphorescent OLEDs

Host	TADF sensitizer	Phosphorescent emitter	EQE <sub>max/1000</sub> <sup>a</sup> (%)	PE <sub>max/1000</sub> <sup>b</sup> ( $\text{lm W}^{-1}$ )	CE <sub>max/1000</sub> <sup>c</sup> ( $\text{Cd A}^{-1}$ )	Ref.
—	PIC-TRZ	Ir(ppy) <sub>3</sub>	—/—	60.0/—	68.0/58.0	17
—	POBICT	PO-01	22.0/21.7	52.6/49.2	—/—	53
—	BICT	PO-01	16.8/16.6	38.4/34.1	—/—	
—	PBICT	PO-01	24.5/24.2	64.5/57.3	—/—	
—	BBICT	PO-01	13.7/13.6	19.7/19.0	—/—	
—	PBICT	Ir(ppy) <sub>3</sub>	23.9/—	—/—	—/—	54
—	OSTFPCN	Ir(MDQ) <sub>2</sub> (acac)	31.2/—	63.6/—	—/—	55
—	OSTFPB	Ir(MDQ) <sub>2</sub> (acac)	29.1/—	60.5/—	—/—	
—	Trz-PhCz	Ir(ppy) <sub>2</sub> (acac)	24.3/22.3	111.8/—	90.0/—	56
—	Trz-PhCz	PO-01	27.3/25.9	98.9/—	80.0/—	
—	Trz-PhCz	Ir(dmppm) <sub>2</sub> (acac)	31.4/29.1	75.5/—	60.0/—	
—	Trz-PhCz	Ir-F-DHBA	30.4/25.9	59.5/—	50.0/—	
—	DMAC-DPS	R-D2	22.2/9.1	—/—	—/—	57
—	4CzDMAC-DPS	R-D2	14.6/10.1	—/—	—/—	
CBP: B4PyMPPM	4CzIPN	PtOEP	21.5/—	—/—	—/—	58

<sup>a</sup> EQE<sub>max/1000</sub> – the maximum EQE and EQEs at 1000  $\text{cd m}^{-2}$ . <sup>b</sup> PE<sub>max/1000</sub> – the maximum power efficiency and PEs at 1000  $\text{cd m}^{-2}$ . <sup>c</sup> CE<sub>max/1000</sub> – the maximum current efficiency and CEs at 1000  $\text{cd m}^{-2}$ .

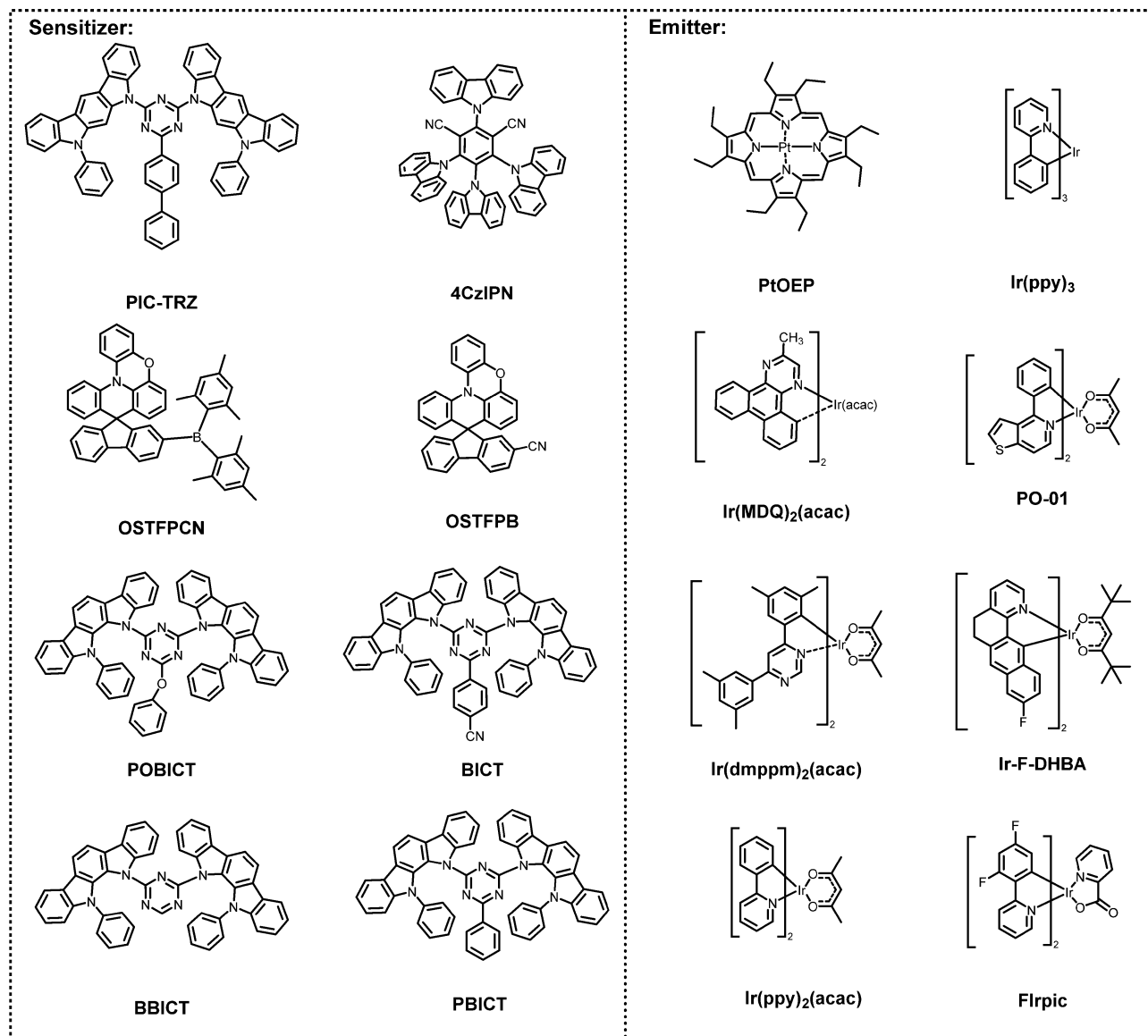


Fig. 7 Chemical structures of TADF sensitizers and phosphorescent emitters.

sensitizer, respectively, to effectively reduce the concentration of the triplet exciton on the emitter through multiple RISC processes.<sup>58</sup> Transient PL spectroscopy found that the film of the CBP:B4PyMPM:4CzIPN:PtOEP had a short phosphorescence decay lifetime. Devices based on these materials achieved a maximum EQE of 22%.

#### TADF-sensitized MR-TADF OLEDs

In the phosphorescence-sensitized MR-TADF OLEDs, the energy transfer reduces the density and lifetime of the triplet exciton in the emitter, achieving an increase in the device lifetime and efficiency and suppression of the efficiency roll-off. However, the maximum EQE is smaller than those of *t*-DABNA and *v*-DABNA-based devices without the sensitizer due to the limitation of the deep-blue phosphorescent material. TADF-sensitized MR-TADF OLEDs realize a further improvement in EQE and lifetime compared to phosphorescence-sensitized MR-TADF devices.

The TADF-sensitized MR-TADF device performances are shown in Table 5. The chemical structures of sensitizers and emitters are shown in Fig. 8.

In the TADF-sensitized MR-TADF devices with the *t*-DABNA emitter, Lee *et al.* introduced DMAC-DPS as a sensitizer.<sup>35</sup> The EQE of sensitized devices is optimized from 25.1% to 31.4% compared to that of non-sensitized devices. Such a significant improvement in EQE is attributed to the increase in PLQY from DPEPO:*t*-DABNA to DPEPO:DMAC-DPS:*t*-DABNA films and close to 100% triplet-to-singlet exciton conversion efficiency.

Although the EQE of DMAC-DPS-sensitized *t*-DABNA devices was significantly improved, the poor stability of the DMAC-DPS material resulted in a device lifetime  $LT_{50}$  of only  $\sim 35$  h at  $100 \text{ cd m}^{-2}$ . Duan *et al.* developed the advanced molecular motif based on a sterically crowded structure with multiple donors and acceptor-type carbazole-biphenyl carbonitrile derivative p4TCzPhBN.<sup>59</sup> The p4TCzPhBN molecules that have



Table 5 Summarized device performances of the TADF-sensitized MR-TADF OLEDs

Host	TADF sensitizers	MR-TADF emitter	EQE <sub>max/1000</sub> <sup>a</sup> (%)	PE <sub>max/1000</sub> <sup>b</sup> (lm W <sup>-1</sup> )	CE <sub>max/1000</sub> <sup>c</sup> (Cd A <sup>-1</sup> )	Ref.
DPEPO	DMAC-DPS	<i>t</i> -DABNA	31.4/19.8	33.6/10.9	32.6/20.9	35
DPEPO	DMAC-DPS	DABNA-1	23.5/15.6	—/—	—/—	
mCPCz	p4TCzPhBN	<i>t</i> -DABNA	32.5/23.2	—/—	—/—	59
oCBP: CNmCBPCN	PPCzTrz	<i>ν</i> -DABNA	33.0/25.2	—/—	39.7/28.9	60
oCBP: CNmCBPCN	PCzTrz	<i>ν</i> -DABNA <sup>d</sup>	33.5/23.8	—/—	35.5/23.4	
oCBP: CNmCBPCN	PPCzTrz	<i>ν</i> -DABNA	29.3/21.4	—/—	32.8/23.6	
oCBP: CNmCBPCN	PCzTrz	<i>ν</i> -DABNA <sup>d</sup>	34.4/21.9	—/—	38.9/24.4	
mCBP	HDT-1	<i>ν</i> -DABNA	27.0/20.0	41.0/16.0	39.0/31.0	62
mCBP	HDT-1	<i>ν</i> -DABNA <sup>e</sup>	41.0/32.0	23.0/10.0	72.0/59.0	
mCBP	4PhCz2BN	<i>ν</i> -DABNA	22.4/17.8	25.0/9.4	25.4/19.1	63
mCPBC	23PCX	<i>ν</i> -DABNA	25.1/23.4	40.4/29.9	—/—	64
mCPBC	33PCX	<i>ν</i> -DABNA	20.6/20.2	24.1/21.7	—/—	
DBFPO	DBA-BFICz	<i>ν</i> -DABNA	38.8/29.1	—/—	30/22.5	65
DBFPO	DBA-BTICz	<i>ν</i> -DABNA	37.3/27.5	—/—	28.3/21.4	
DBFPO	<i>m</i> MDBA-DI	<i>t</i> -Bu- <i>ν</i> -DABNA	39.1/34.3	—/—	30.3/26.6	66
DBFPO	<i>p</i> MDBA-DI	<i>t</i> -Bu- <i>ν</i> -DABNA	37.9/34.8	—/—	36.2/33.0	
PPF	dCz-Xo-TRZ	<i>ν</i> -DABNA	33.5/27.3	35.8/—	37.6/—	71
PPF	<i>m</i> Cz-Xo-TRZ	<i>ν</i> -DABNA	24.5/19.2	24.1/—	27.5/—	
mCPBP	5TCzBN	2F-BN	22.0/15.0	69.8/38.1	—/—	79
mCPBP	5TCzBN	3F-BN	22.7/21.1	72.3/45.9	—/—	
mCPBP	5TCzBN	4F-BN	20.9/16.4	51.3/29.4	—/—	
mCPBP	CTPCF3	2F-BN	33.1/27.0	76.1/43.9	—/—	73
mCPBP	CNCTPCF3	3F-BN	25.6/14.2	62.4/22.7	—/—	
mCPBP	TCTPCF3	4F-BN	23.2/18.8	46.4/29.8	—/—	
mCPBC	1CTF	AZA-BN	27.6/20.1	—/—	—/—	74
mCPBC	2CTF	AZA-BN	30.3/22.8	—/—	—/—	
mCPBC	3CTF	AZA-BN	31.6/24.5	—/—	—/—	
mCBP	HDT-1	CzBNCz	21.9/19.8	47.8/—	42.6/—	75
mCBP	HDT-1	CzBN	20.6/17	40.1/—	38.3/—	
mCBP	HDT-1	DABNA-2	24.1/18.4	45.4/—	46.3/—	
mCBP	HDT-1	CzBN	22.0/17.1	38.2/—	48.7/—	76
mCBP	HDT-1	CzBNPyT	19.4/15.1	37.1/—	41.5/—	
DMIC-TRZ	BNSeSe	BN3	40.5/32.4	205.8/197.7	164.5/162.4	18

<sup>a</sup> EQE<sub>max/1000</sub> – the maximum EQE and EQEs at 1000 cd m<sup>-2</sup>. <sup>b</sup> PE<sub>max/1000</sub> – the maximum power efficiency and PEs at 1000 cd m<sup>-2</sup>. <sup>c</sup> CE<sub>max/1000</sub> – the maximum current efficiency and CEs at 1000 cd m<sup>-2</sup>. <sup>d</sup> The top-emitting devices. <sup>e</sup> The two-unit-stacked tandem devices.

unique molecular motifs with linearly localized donors and acceptors exhibited the most efficient TADF characteristics with a high RISC rate of  $2.36 \times 10^6 \text{ s}^{-1}$ . The sensitized device with *t*-DABNA as the emitter had the maximum EQE of 32.5%. The  $T_{80}$  of 60 h was obtained at 1000 cd m<sup>-2</sup>, which was six times higher than the device without the sensitizer. At an initial luminance of 100 cd m<sup>-2</sup>, the extrapolated blue OLED lifetime exceeded 3000 h. The long lifetime mainly benefits from the fast RISC rate of the sensitizer, which promotes the up-conversion of triplet excitons to single excitons and increases the exciton utilization.

TADF materials have also shown excellent electroluminescence performance as sensitizers for *ν*-DABNA molecules, especially in the lifetime and EQE. In 2021, Lee *et al.* constructed the triplet exciton-distributed TADF (TED-TADF) device with a low-triplet energy host.<sup>60,61</sup> The triplet energy of the host is slightly lower than that of the sensitizer and higher than that of the emitter. Compared with the high triplet energy of the host, the triplet excitons in the host with the low triplet energy can be recycled by the TADF sensitizer, thus suppressing the annihilation of triplet excitons while ensuring the stability of the material. Two deep-blue-emitting TADF materials, PPCzTrz and PCzTrz, were synthesized and selected as sensitizers. When employing these materials to sensitize the *ν*-DABNA emitter, the corresponding device realized maximum EQEs of  $33 \pm 0.3\%$  and  $33.5 \pm 0.1\%$ , and at 1000 cd m<sup>-2</sup> of  $25.2 \pm 0.8\%$  and  $23.8 \pm 0.2\%$ , respectively.

The high EQE of the TED-TADF device can be explained by the high PLQY of the PPCzTrz:*ν*-DABNA-doped film. The device lifetimes ( $LT_{50}$ ) were  $151 \pm 3 \text{ h}$  and  $112 \pm 3 \text{ h}$  (at an initial luminance of 1000 cd m<sup>-2</sup>). To further improve the efficiency, a top-emitting device was developed, and the EQEs of the PPCzTrz and PCzTrz devices reached  $43.8 \pm 1.4\%$  and  $52.9 \pm 1.5\%$  with a CIE<sub>y</sub> value of 0.09 because of the reflecting microcavity effect, achieving the CCE values of  $364 \pm 10 \text{ cd A}^{-1}$  and  $432 \pm 11 \text{ cd A}^{-1}$ , respectively. The results represent one of the highest EQE and the longest device lifetimes for deep-blue OLEDs with *y* color coordinates below 0.10.

Hatakeyama and Adachi *et al.* also reported efficient and stable deep-blue OLEDs, in which the electrically generated energy of the sky-blue TADF sensitizer called the hetero-donor-type (HDT) TADF is exothermically transferred to the excited state of the deep-blue emitter.<sup>61,62</sup> The hetero-donor-type TADF molecules named TPh2Cz2DPhCzBN (HDT-1) with a sky-blue emission peak, fast  $k_{\text{RISC}}$ , high PLQY, and short delayed lifetime were synthesized to sensitize *ν*-DABNA. The sensitizer can be red-shifted relative to the emitter as the charge-transfer excited state of the TADF sensitizer results in a broad distribution of energy states and a small Stokes shift of *ν*-DABNA. The device based on this material has obtained a maximum EQE of 27%, a remaining high EQE of 20% even at 1000 cd m<sup>-2</sup>, and an  $LT_{95}$  of over 10 h. The two-unit stacked tandem OLED was

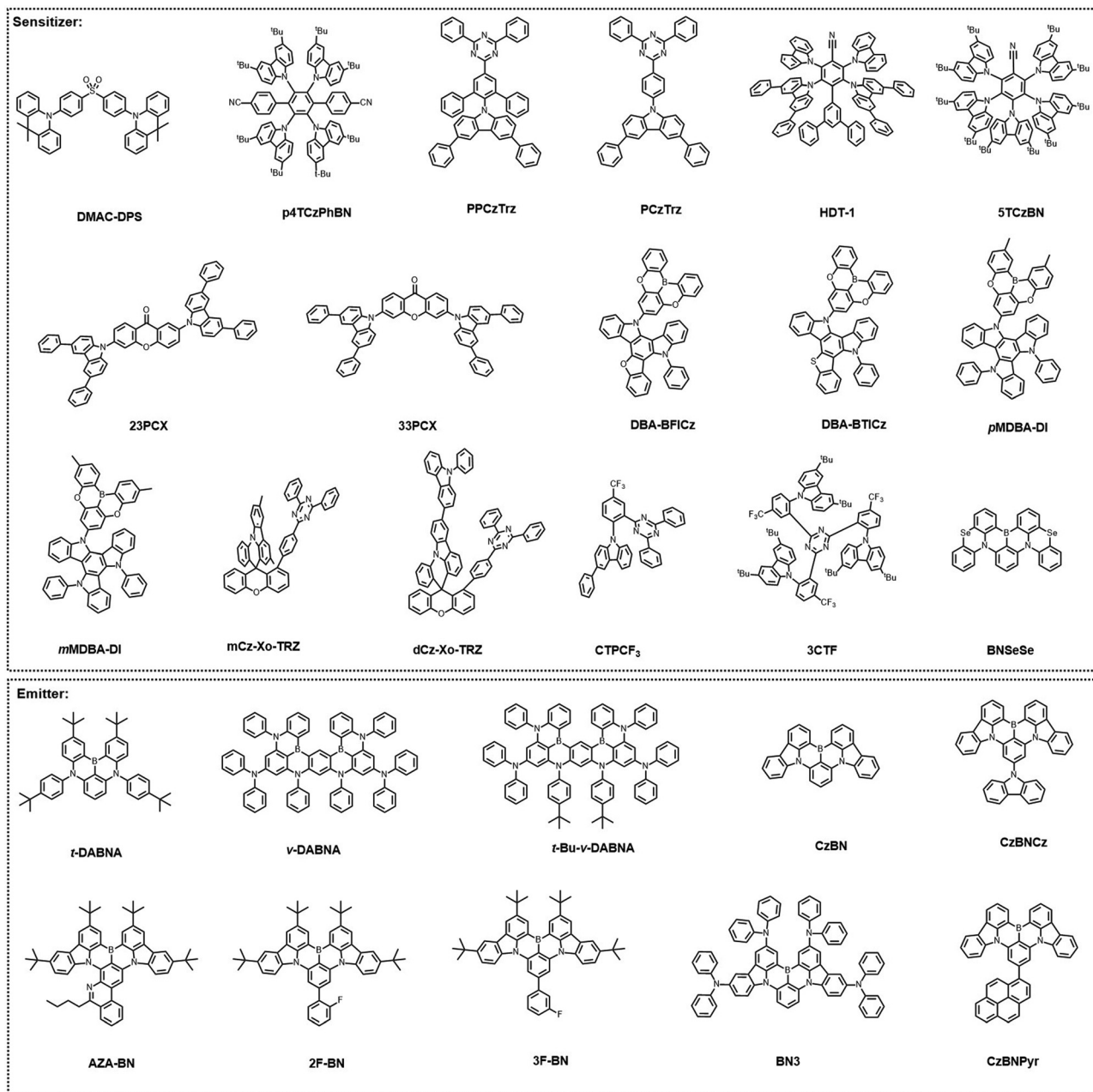


Fig. 8 Chemical structures of TADF sensitizers and MR-TADF emitters.

implemented to improve the device performance further. The device exhibits an outstanding EQE of 41% with an improved  $LT_{95}$  of 18 h at  $1000 \text{ cd m}^{-2}$ .

The HDT-1 sensitized  $\nu$ -BABNA OLED achieved an extended lifetime compared to non-sensitized devices, but HDT-1 also exhibited incomplete energy transfer to  $\nu$ -DABNA. Recently, Adachi *et al.* developed multiple donor and acceptor blue TADF materials to sensitize  $\nu$ -DABNA.<sup>63</sup> The four donors and two acceptors (4PhCz2BN) exhibited a fast RISC process ( $k_{\text{RISC}} > 10^6 \text{ s}^{-1}$ ) resulting from the dense alignments of  $^1\text{CT}$ ,  $^3\text{CT}$ , and  $^3\text{LE}$ . The material also exhibited  $k_{\text{r}} > 10^7 \text{ s}^{-1}$ . The sensitized devices had a maximum EQE of 22.4% with CIE coordinates (0.13, 0.15).

The stability of the molecular structure also exerts a positive influence on the extended lifetime of the device. A novel TADF structure, D-void-A, was designed by Duan *et al.*<sup>64</sup> The D and A groups are connected through a vacant position in the  $\pi$ -principal chain of A (no HOMO-assigned carbon atom in the A group), which can inhibit the binding of the HOMO between D and A, while the deeper HOMO energy level of the acceptor becomes the energy level of the molecule, resulting in a larger blue emission energy gap. phCz is connected to the C1, C2, and C3 positions of the Xo group, where the C3 position has a deeper HOMO energy level. Using these molecules as a sensitizer for  $\nu$ -DABNA, the maximum EQE of the devices based on 23PCX and 33PCX were 25.1% and 20.6%, respectively.

The device with 33PCX as a sensitizer exhibited worse performance mainly due to the larger  $\Delta E_{ST}$ . It is worth mentioning that  $LT_{95}$  of  $\approx 13$  and  $\approx 15$  h were recorded for devices with 33PCX and 23PCX, which can be compared with the OLED lifetime of Adachi and Lee *et al.* This work provides that the highly efficient and stable blue TADF emitters should take TADF molecules with good stability into consideration.

The EQE of TADF-sensitized  $\nu$ -DABNA OLEDs needs to be further enhanced to compete with  $\nu$ -DABNA-based OLEDs. The recent work reported by Kwon *et al.* gave an idea of how to appropriately design TADF sensitizers to achieve a high EQE.<sup>65,66</sup> In 2021, the group designed and synthesized two deep-blue TADF materials, DBA-BFIC and DBA-BTICz. The DBA moiety is one of the ideal acceptors for blue molecules, while the BFICz and BTICz donors were modified with the heteroatoms of oxygen and sulfur on the rigid donor to reduce the donor strength, increasing the spectral overlap area between the TADF material and the  $\nu$ -DABNA emitter. The corresponding deep-blue devices exhibited the maximum EQEs of 38% and 37.3%, respectively. Another TADF-sensitized device similar to this work exhibited a higher performance. The new TADF materials were synthesized, namely, *p*MDBA-DI and *m*MDBA-DI, with methyl substituted at the heteroatom's *para* and *meta* positions to reduce the acceptor strength. To effectively inhibit the DET process, *tert*-butyl groups were introduced on the  $\nu$ -DABNA to reduce aggregation quenching and enhance the PLQY. Utilizing the *m*MDBA-DI sensitized *t*-Bu- $\nu$ -DABNA OLED results in a record-high EQE of 39.1%. Furthermore, the *p*MDBA-DI sensitized device with the DCzPy host exhibited a device lifetime of 440 h ( $LT_{50}$ ) at an initial luminance of 1000  $\text{cd m}^{-2}$ . Such high efficiency of the two reported works is mainly attributed to the high horizontal orientation factor and the PLQY of the TADF sensitizer, the low doping concentration, and the sufficient energy transfer between the sensitizer and the emitter, as well as the additional triplet excitons obtaining from the DET process and charge trapping on the emitter.

The through space charge transfer (TSCT) TADF materials also exhibit interesting properties in terms of sensitizers due to their extremely small  $\Delta E_{ST}$  and dipole moments, but the  $k_r$  and  $k_{RISC}$  of the TSCT-TADF materials cannot be balanced.<sup>67-70</sup> The group constructed a novel TSCT sensitizer material using the Xo group, mCz-Xo-TRZ, and dCz-Xo-TRZ.<sup>71</sup> Benefiting from the short D-A distance, the device has a radiative decay rate close to  $10^7 \text{ s}^{-1}$  and achieves a high PLQY. The dCz-Xo-TRZ-based sensitized device has a maximum EQE of 34.7% when using  $\nu$ -DABNA as the emitter. In addition, the device exhibits a small efficiency roll-off (27.6% at 10 000  $\text{cd m}^{-2}$ ), and the fast FET rate promotes exciton transfer between the sensitizer and the emitter, alleviating the efficiency roll-off of the device.

In the case of the green color, Duan *et al.* synthesized the well-known green-emitting MR-TADF core (BCz-BN) by replacing the diphenylamine donor in the DABNA core with a carbazole.<sup>72</sup> Based on the BCz-BN core, a range of green MR-TADF materials are designed and the corresponding sensitizers are selected or engineered to match them. In 2019, they introduced electron-absorbing groups at the *para*-position of BCz-BN to design

MR-TADF materials 2F-BN, 3F-BN, and 4F-BN. The OLED utilizing 5TCzBN as the sensitizer and 3F-BN as the emitter showed a maximum EQE of 22.7%, a maximum PE of 72.3  $\text{lm W}^{-1}$  and CIE coordinates of (0.20,0.58). And the lifetime  $LT_{90}$  based on 2F-BN reached 45.76 h, which is one of the most stable green emitters available.

In 2020, Duan *et al.* made the combination of TSCT and TBCT by designing donor-acceptor structures CTPCF3, CNCTPCF3, and TCTPCF3 with the neighbour arrangement.<sup>73</sup> CTPCF3, with the highest  $k_{RISC}$ , achieves the shortest lifetime of the delayed part and the relatively small molecular dipole moment. The highest EQE of 33.1% was achieved for the device with CTPCF3 selected as the sensitizer while again employing 2F-BN as the emitter, which far exceeds the rest of the work. This high efficiency can be attributed to the high PLQY resulting from the fast FET process. It is noteworthy that the TADF sensitizer uses the same emission spectrum as 2F-BN, which is not pursuing a large overlap with the absorption spectrum of the MR-TADF emitter. In addition, the group built on this works to design a TADF molecule containing ortho-linked multiple donor-acceptor motifs.<sup>74</sup> Owing to the maximum oscillator strength value of 3CTF and its dense excited state manifold near  $S_1$  and  $T_1$  states, 3CTF achieves both high  $k_r$  and  $k_{RISC}$ . Unfortunately, the device efficiency is unsatisfactory owing to the low external coupling factor. They have hence applied it as a sensitizer for AZA-BN, reasonably avoiding that disadvantage. The corresponding green-sensitized OLED achieves a high EQE of 31.6% thanks to its high RISC rate. This work has demonstrated that the ideal sensitizer should have an efficient RISC rate and a high PLQY to ensure sufficient exciton harvesting.

The energy level matching between the sensitizer and the emitter contributes significantly to the device's lifetime. Adachi *et al.* achieved a low-efficiency roll-off and a long lifetime by modulating the HOMO energy level between the sensitizer and the emitter.<sup>75</sup> The BN compounds with carbazole substitution (CzBN and CzBNCz) with deeper HOMO energy levels were synthesized, and the DABNA-2 material was chosen for comparison. Sensitized devices were produced employing TPh2Cz2DPhCzBN as the sensitizer, where the  $LT_{90}$  of CzBN and CzBNCz as the emitters, was 39.3 and 28.8 h at 1000  $\text{cd m}^{-2}$ , respectively, approximately twice those of DABNA-2 based devices. The analysis of the HOMO energy levels reveals that the energy levels of 5.56 and 5.71 eV for CzBN and CzBNCz, respectively, are closer to the sensitizer than that of 5.38 eV for DABNA-2. Meanwhile, the transient electroluminescence spectra confirm that the smaller HOMO energy level difference reduces the hole trapping in the luminescent layer. The reduced HOMO energy level differential also results in a decrease in the driving voltage and efficiency roll-off. Recently, Adachi *et al.* had also designed stable sensitized devices employing HDT-1 as the sensitizer.<sup>76</sup> They designed CzBNPPr based on the CzBN molecule and the pyrene unit. CzBNPPr does not possess TADF activity owing to the introduction of the pyrene unit. Sensitized OLEDs with HDT-1 as the sensitizer showed excellent device lifetime ( $LT_{95} = 40$  h) because of the low- $T_1$  emitter.

In addition, to be an efficient emitter, the devices using MR-TADF materials as the sensitizer also show outstanding

performance. Very recently, Yang *et al.* synthesized BNSeSe by embedding the non-metallic heavy atom Se atom into the multiple resonance skeleton.<sup>18</sup> The heavy atom effect significantly increased the coupling between singlet and triplet orbits, achieving a high RISC rate and a high PLQY. Due to the short delay fluorescence lifetime, high PLQY, and excellent electroluminescence performance, BNSeSe was conceived and selected as the sensitizer of the yellow-emitting MR-TADF transmitter BN3. The EQE of the corresponding device exceeded 40%, the maximum PE exceeded 200 lm W<sup>-1</sup>, and the maximum brightness was close to 200 000 cd m<sup>-2</sup>. This work was the first to design high-efficiency, low roll-off, high-purity OLEDs employing MR-TADF as the sensitizer.

TADF-sensitized OLEDs are more conducive to achieve the high EQE device than phosphorescence-sensitized OLEDs. Apart from the high PLQY value, the rapid RISC process is also key to improving EQE. The fast FET process also promotes exciton utilization and thus efficiency. In addition, TADF sensitizers are more favourable than phosphorescent sensitizers for the application of highly efficient deep-blue sensitized OLEDs.

## Exciplex-sensitized OLEDs

The exciplex is not only an efficient emitter but also an excellent sensitizer as the energy transfer medium. The exciplex usually has a TADF nature. Since the HOMO and LUMO orbitals of the exciplexes are essentially completely distributed molecules, the spatial separation between the electron donor and the electron acceptor is very large, resulting in a very small  $\Delta E_{ST}$  and a quick RISC rate. The mechanism of the exciplex is similar to that of the TADF material as a sensitizer. Still, the exciplex sensitizer is usually engineered with a large HOMO–LUMO offset to have a small  $\Delta E_{ST}$  close to 0 eV that facilitates faster harvesting of triplet state excitons.<sup>26</sup> The exciplex-sensitized device performances are shown in Table 6. The chemical structures of sensitizers and emitters are shown in Fig. 9.

In 2015, Lee *et al.* prepared the first OLED using an exciplex host to sensitize the fluorescent dopant.<sup>16</sup> DPTPCz and TAPC were mixed 1 : 1 (by weight) to form the exciplex host. C545T was selected as the fluorescent dopant. The TAPC:DPTPCz exciplex had a small  $\Delta E_{ST}$ , a high PLQY, and an efficient RISC. The absorption spectrum of C545T overlaps well with the PL spectra of TAPC:DPTPCz. Unfortunately, the energy transfer between the excipient and the fluorescent dopant was insufficient,

as the weak DPTPCz emission in the mixed films was observed. The OLEDs based on the exciplex sensitizer showed a maximum EQE of 14.5%, a maximum CE of 44 cd A<sup>-1</sup>, and a maximum PE of 46.1 lm W<sup>-1</sup>, which harvested nearly 100% of triplets.

The exciplex as a sensitizer can also increase the EQE of the exciplex emitter. In 2019, Lee *et al.* constructed a ternary exciplex system using the p-type donor, a carbazole-derived 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl (CDBP) and the n-type acceptor, 2,4,6-tris[3-(diphenylphosphinyl) phenyl]-1,3,5-triazine (PO-T2T), to form a high energy exciplex.<sup>77</sup> The n-type acceptor was mixed with the donor–acceptor TADF emitter DABNA-1 to generate a low-energy exciplex. Molecular dynamics simulations demonstrated the good dispersibility of the PO-T2T:DABNA-1 exciplex. The emission peak of the CDBP:PO-T2T film was 480 nm, which overlapped with the absorption peak of the PO-T2T:DABNA-1 exciplex (between 380 and 480 nm). The OLED based on a ternary exciplex film exhibited a high EQE of 17.8%. Similarly, Zhang *et al.* designed a donor that facilitates solution processing, 4-(9-(perfluoropyridin-4-yl)-9H-fluoren-9-yl)-N,N-diphenylamine, TPA-3, which forms green exciplexes with the acceptor PO-T2T.<sup>78</sup> Two donors, 3CzFDPhTz (3-(9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-fluoren-9-yl)-9-phenyl-9H-carbazole) and 9PhFDPhTz (9-(4-(9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H-fluoren-9-yl) phenyl)-9H-carbazole), with PO-T2T, are forming the sky blue exciplex. By analyzing the transient photoluminescence decay curve, the ternary exciplex has a faster RISC rate than the binary exciplex, while the additional RISC process makes more use of the triplet exciton. The solution-processed exciplex OLEDs based on the interfacial exciplex provided maximum EQEs of 18.8% and 24.0%, respectively.

In addition to the single-host exciplex sensitizing system, a high EQE in the fluorescent OLED was achieved using two exciplexes as the host and the sensitizer of the fluorescent emitter. Lee *et al.* developed the cascade singlet harvesting (CSH) OLEDs using the POT2T:CDBP high energy exciplex as the host, the POT2T:DABNA-1 low energy exciplex as the sensitizer, and TBRb as the emitter.<sup>79</sup> Through analysis of singlet and triplet energy transfer between the exciton and TBRb, triplet exciton quenching by Dexter energy transfer, and molecular dynamics simulations indicated that the CSH mechanism suppressed the DET process. The maximum EQE of the device was 18.7% for DABNA-1 and TBRb at 10 and 0.5 wt%. Replacing DABNA-1 with *t*-DABNA, the maximum EQE of the TBRb-doped POT2T:CDBP : *t*-DABNA (45 : 45 : 10) exciplex device was further

**Table 6** Summarized device performances of the exciplex-sensitized OLEDs

Exciplex host	Exciplex sensitizer	Emitter	EQE <sub>max/1000</sub> <sup>a</sup> (%)	PE <sub>max/1000</sub> <sup>b</sup> (lm W <sup>-1</sup> )	CE <sub>max/1000</sub> <sup>c</sup> (Cd A <sup>-1</sup> )	Ref.
—	TAPC:DPTPCz	C545T	14.5/—	46.1/—	44.0/—	16
—	CDBP:PO-T2T	PO-T2T:DABNA-1	17.5/15	—/—	60.9/51.1	77
—	TPA-3:3CzFDPhTz	3CzFDPhTz:PO-T2T	18.8/8.9	43.0/16.3	63.0/29.6	78
—	TPA-3:9CzFDPhTz	9CzFDPhTz:PO-T2T	—/—	61.4/24.7	78.2/32.7	—
CDBP:PO-T2T	PO-T2T:DABNA-1	TBRb	18.7/18.0	46.7/36	64.8/62.5	79
—	Tris-PCz:3Cz-TRZ	<i>ν</i> -DABNA	19.0/18.0	—/—	—/—	80

<sup>a</sup> EQE<sub>max/1000</sub> – the maximum EQE and EQEs at 1000 cd m<sup>-2</sup>. <sup>b</sup> PE<sub>max/1000</sub> – the maximum power efficiency and PEs at 1000 cd m<sup>-2</sup>. <sup>c</sup> CE<sub>max/1000</sub> – the maximum current efficiency and CEs at 1000 cd m<sup>-2</sup>.



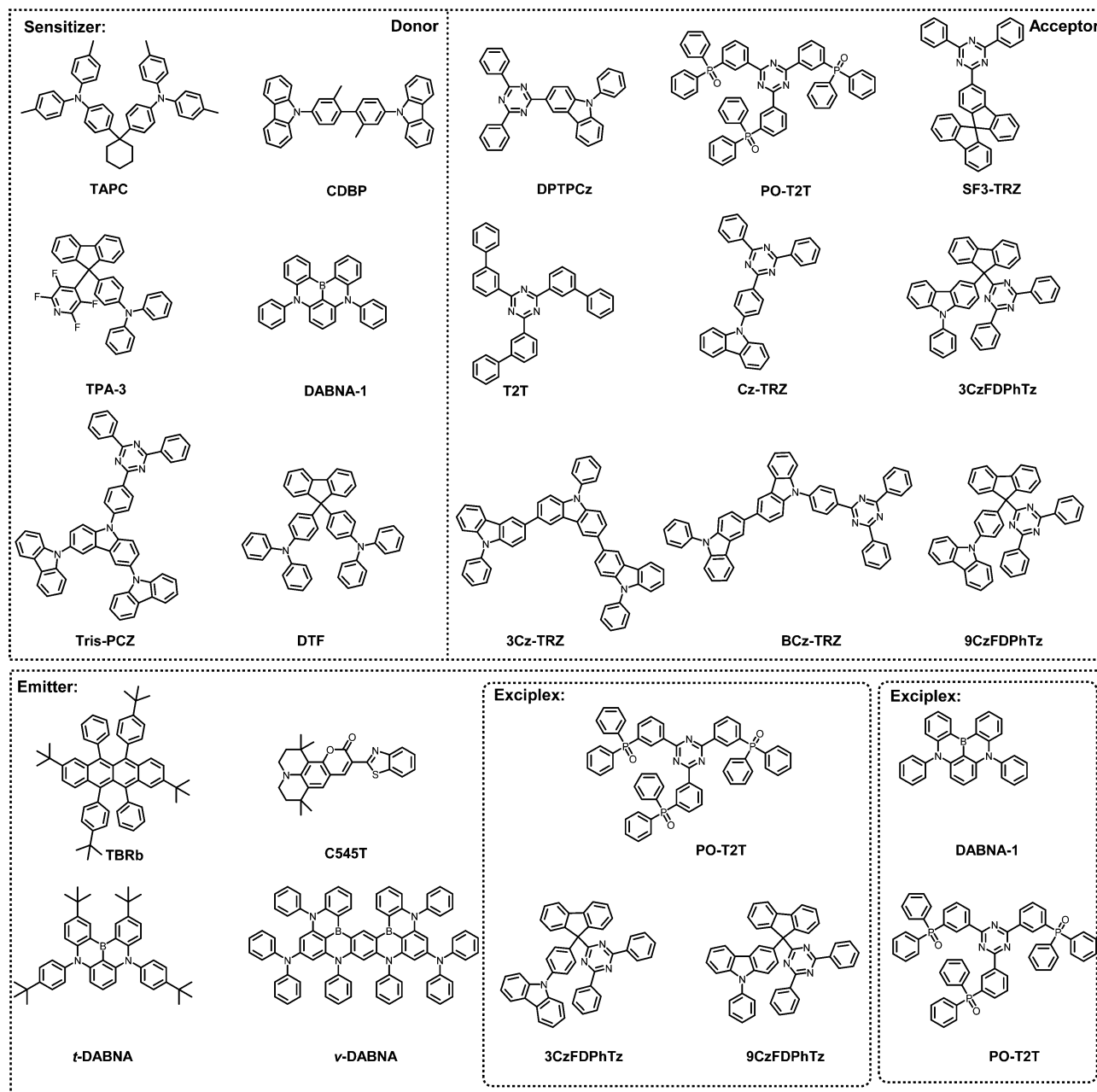


Fig. 9 Chemical structures of exciplex sensitizers and corresponding emitters.

increased to 19.9% in comparison with 10.4% of the common exciplex based fluorescent OLEDs.

Despite the improved EQE achieved by the exciplex-based system, the operational device stability of exciplex-based OLEDs is still far from practical applications. Adachi *et al.* have enhanced the device lifetime by rationally selecting TADF-type electron acceptors.<sup>80</sup> When the TADF material is used as an acceptor for the exciplex, the recycling of triplet excitons between the TADF-type electron acceptor and the exciplex is carried out through the RISC process, thus reducing the density of triplet excitons. 9,9',9''-Triphenyl-9H,9'H,9''H-3,3':6',6''-tercarbazole (Tris-PCz) with a strong electron-donating group of tricarbazole had been selected as a donor molecule. The

conventional acceptors, 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T) and 2-(9,9'-spirobi[fluoren]-3-yl)-4,6-diphenyl-1,3,5-triazine (SF3-TRZ), bipolar-type acceptor, 9-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-9H-carbazole (Cz-TRZ), and TADF-type acceptors, 9-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-9'-phenyl-9H,9'H-3,3'-bicarbazole (BCz-TRZ) and 3Cz-TRZ were compared with each other. It was found that the devices with the addition of the electron-donating group and those with TADF-type acceptors had significantly longer lifetimes. Compared to conventional and bipolar acceptors, TADF-type acceptors have a lower cumulative triplet density during OLED operation, resulting in a more stable device over the long term. The *v*-DABNA doped OLED achieved an EQE of 19%. The blue OLED maintains stability after

incorporating  $\nu$ -DABNA (LT<sub>50</sub> over 300 h at higher luminance). Regrettably, the energy transfer between the exciplex and  $\nu$ -DABNA is not sufficient, which reflects the potential of this system to achieve highly stable exciplex-sensitized devices.

## Conclusion and outlook

Sensitized OLEDs have been developed over the last several decades, and tremendous progress has been made accompanying the evolution of new emitters. In contrast to fluorescent, phosphorescent, and MR-TADF OLEDs, sensitized OLEDs have developed a new path to devices with high efficiency, long lifetimes, better color purity, and low-efficiency roll-off.

In terms of sensitizers for sensitized devices, phosphorescence-sensitized OLEDs exhibit a lower EQE value than TADF-sensitized devices owing to the lack of the corresponding high-performance sensitizers. In the case of emitters for sensitized devices, the EQE value of the sensitized fluorescent OLEDs is generally lower than that of the phosphorescent, TADF, or exciplex OLEDs, because of the larger energy loss, such as the incomplete FET process, the DET process, and direct charge recombination on the emitter. In addition, sensitized fluorescent OLEDs with blue emission still require further research owing to the large Stokes shift of the fluorescent material and the poor performance of the blue phosphorescent, TADF, and exciplex sensitizers. MR-TADF materials with small Stokes shifts and triplet exciton availability are better suited than fluorescent materials as emitters for blue-sensitized devices. The maximum EQE values for sensitized MR-TADF OLEDs have surpassed 40% to date. However, the lifetime of the sensitized MR-TADF OLEDs still needs a further extension for commercial applications compared to those of the fluorescent and PhOLEDs. The device lifetime is closely related to the lifetime and density of the triplet exciton, with singlet–triplet annihilation, triplet–triplet annihilation, and triplet–polariton annihilation being the main processes which reduce the device lifetime. In addition, the stability of the materials, both sensitizers and emitters, is also necessary. The HOMO and LUMO energy level matching of the device also affects the lifetime to some extent.

The EQE and lifetime of exciplex-sensitized devices are less satisfactory than those of phosphorescent and TADF-sensitized devices. However, multiple sensitizing processes using exciplexes or TADF materials as the host in combination with TADF and phosphorescent sensitizers exhibit significant device performance and lifetime due to the full harnessing of triplet exciton and increased exciton transfer channels.

In the pursuit of high-performance sensitized OLEDs, we should take into account the sensitizer and energy transfer efficiency. An ideal sensitizer should have a high PLQY, short excited state lifetime, and low molecular dipole moment. A high RISC process is highly desired by TADF or exciplex sensitizers to suppress exciton annihilation. Next, efficient energy transfer efficiency should occur between the sensitizer and the emitter. A large degree of overlap between the sensitizer's emission spectrum and the emitter's absorption spectrum

is necessary. Notably, this has not meant that a small degree of overlap would not allow for efficient energy transfer, especially for MR-TADFs with small Stokes shifts. The DET process is generally a pathway for exciton loss, which can be avoided by designing molecules with large steric groups to modulate the spatial distance between the sensitizers and the emitters. Moreover, the residual emission of the sensitizer is attributed to incomplete energy transfer. We can avoid the effect of residual emission by increasing the spectral overlap between the sensitizer and the emitter or by choosing an emitter with a small Stokes shift, which effectively increases the energy transfer efficiency.

Despite the great achievements in sensitized devices, efficient sensitized OLEDs still present challenging problems. In the future, the design strategy of efficient phosphorescent, TADF, and exciplex sensitizers should be paid more attention. In addition, energy transfer needs to be further investigated in detail to obtain high-performance sensitized OLEDs. In summary, we believe that sensitized OLEDs can achieve significant breakthroughs in efficiency and lifetime to enable commercial utilization.

## Conflicts of interest

There are no conflicts to declare.

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