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Review

# The application of charge transfer host based exciplex and thermally activated delayed fluorescence materials in organic light-emitting diodes



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## ABSTRACT

Here, we review systematically the applications of exciplex and thermally activated delayed fluorescence (TADF) materials as the host in organic light-emitting diodes (OLEDs), who is the charge transfer host based intermolecular and intra-molecular, respectively. Exciplex and TADF materials present many advantages of natural bipolarity, small singlet-triplet splitting energy and low driving voltage to act as the host rather than emitter. The applications of exciplex and TADF materials as the host in phosphorescent, fluorescent and white OLEDs are given and new challenges, suggestions are also provided finally for further research and potential development of this area.

## 1. Introduction

In 2012, the two papers published on Nature Photonics of exciplex based inter-molecular charge transfer and Nature of thermally activated delayed fluorescence (TADF) materials based intra-molecular charge transfer, respectively, made the application of TADF mechanism in organic light-emitting diodes (OLEDs) walking into the view of researchers indeed, which came from the same group of Adachi [1,2]. The core of TADF is the reverse intersystem crossing (RISC), which makes the triplet excitons transferring into singlet excitons and then producing the light-emitting of delayed fluorescence (or called E-type delayed fluorescence). The TADF mechanism exists in exciplex or TADF materials and could improve the electroluminescence (EL) efficiency largely. The external quantum efficiency (EQE) of exciplex and TADF materials all broke the fluorescent quantum efficiency upper limit and reached to 5.4% and 19.3% in that two papers, respectively. After that, many highly efficient and various colors light-emitting exciplex and TADF materials were designed out and rapidly became the research focus [3–7].

But in this review, we pay close attention to another application of exciplex and TADF materials in OLEDs, which is as the host to transfer energy. We know that almost all the highly efficient OLEDs adopt the host-guest doped system, so the host materials are very important in

OLEDs. In generally, the host materials require high singlet and triplet excited state energy, well bipolar electrons and holes transport ability, and matched highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level to transport layer. By the exploration of exciplex formation process and TADF materials design principle, we consider the exciplex and TADF materials are more suitable as the host to sensitize dopant, including traditional fluorescent, phosphorescent and TADF dopants. Exciplex and TADF materials present natural bipolar charge transport, which stem from the mixed donor and acceptor materials in exciplex and connected donor and acceptor units in TADF materials. The donor and acceptor usually exhibit excellent electrons and holes transport ability, respectively. And the intrinsic small singlet and triplet excited state energy splitting  $(\Delta E_{ST})$  make the exciplex and TADF materials conduct the similar singlet and triplet energy level, which have a better energy transfer efficiency to dopant. Many works had been made to employ the exciplex and TADF materials as the host and our group also did much effort to explore their application in host.

In the section 2 of the review, we focus on the formation process of exciplex, and the design principle of TADF materials. Further, the advantages of exciplex and TADF materials as the host would be listed item by item in section 3. Next a mass of applications of exciplex and TADF materials as the host in monochromatic OLEDs and white OLEDs

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(WOLEDs) are introduced to clarify deeply in section 4 and 5. A conclusion and outlook are also given in the final section.

## 2. Exciplex and TADF materials

#### 2.1. Exciplex

There exist many organic-organic interfaces in organic photoelectric devices no matter layer by layer flat-heterojunction or mixed bulk-heterjunction. Among these contiguous organic molecules, inevitable molecular interaction would produce the new excited state, which is defined as charge transfer excited state and the corresponding excitons are called charge transfer excited state and the corresponding excitons are called charge transfer excited. The charge transfer excited state could also be divided as charge transfer singlet excited state and charge transfer triplet excited state. The like molecular interaction forms excimer and the exciplex come from the interaction between unlike molecules. In generally, the exciplex present low charge transfer excited state compared to the donor or acceptor monomer, so an obvious red shift could be observed from the PL or EL spectra through the exciplex excitons deexcitation process of radiative transition.

However, exciplex was unwelcome in OLEDs in the early stage due to the low device performances caused by low utilization ratio of excitons, so that researchers did much works to avoid the appearance of exciplex in OLEDs. However, Adachi group firstly exploited high efficiency exciplex emission of 5.4% EQE with 4,4',4"-tris[3-methylphenyl (phenyl)amino]triphenylamine (m-MTDATA) as the donor and tris-[3-(3-pyridyl)mesityl]borane (3TPYMB) as the acceptor, respectively [1]. And more and more high efficiency exciplex were developed sequentially after that [8-13]. The formation process of exciplex under electrical excitation are showed in Fig. 1. The excitons are produced from the direct recombination between electrons on LUMO<sub>acceptor</sub> and holes on  $HOMO_{donor}$ , respectively. The offsets between  $\dot{LUMO_{donor}}/LU$ - $\mathrm{MO}_{\mathrm{acceptor}}$  and  $\mathrm{HOMO}_{\mathrm{donor}}/\mathrm{HOMO}_{\mathrm{acceptor}}$  play the key role to form the exciplex and the offset value fixed at  $\sim 0.4 \text{ eV}$  is more suitable to produce the efficient exciplex emission because of the better charge accumulation and higher radiative transition efficiency. As mentioned above, the exciplex excitons could also be divided into singlet excitons of 25% and triplet excitons of 75%, which are produced on charge transfer singlet excited state and charge transfer triplet excited state, respectively. So similar to the monomer emission molecule, there also exist the  $\Delta E_{ST}$  in exciplex. The highly efficient exciplex is always accompanied by small  $\Delta E_{ST}$ , which make the RISC process occur. Thereby,



Fig. 1. The formation and emission processes of exciplex under electrical excitation. PF: prompt fluorescence; DF: delayed fluorescence.

the TADF caused by RISC contribute to the high efficiency exciplex with delayed fluorescence. While the higher singlet and triplet excited state energy of donor and acceptor than exciplex singlet and triplet excited state energy is another key factor to achieve high efficiency exciplex OLEDs because the suppressive reverse energy transfer from exciplex to donor or acceptor molecules. But a very important point should be stated, not all the exciplexes have the TADF characteristic, that means the RISC process could not occur in all the exciplexes. So we maybe separate exciplexes from common exciplex and TADF exciplex.

## 2.2. TADF materials

TADF materials are called as the third generation light-emitting materials used in OLEDs, which combine the advantages of traditional fluorescent and phosphorescent materials. Pure organic molecules without heavy metal make TADF materials the low cost, and almost 100% internal quantum efficiency (IQE) could also be realized due to the efficient triplet excitons up-conversion. Different from the exciplex with mixed donor and acceptor molecules, the TADF materials are monomer molecules, however, also be designed by combining the donor segment and acceptor segment in one molecule. That means that the emission of TADF materials derives from the charge transfer between donor and acceptor segment. Furthermore, two key points should be considered to design the pure organic TADF molecules: one is the separate donor and accepter segment to achieve the spatially separated HOMO and LUMO energy level, which could result in small  $\Delta E_{ST}$  and efficient RISC process; the other is to utilize the steric hindrance to strengthen molecular structural rigidity, hence to enhance photoluminescence (PL) radiative luminescent efficiency.

Now, following the design principle above, more and more excellent TADF materials based on kinds of derivatives are explored and the EQE could reach the level of phosphorescent OLEDs [14–17]. Under electric excitation, the 25% singlet excitons and 75% triplet excitons are produced on singlet and triplet excited state, respectively. The 25% singlet excitons would radiative transition directly to obtain the prompt fluorescence and 75% triplet excitons could up-convert to singlet excitons by RISC from the lowest triplet excited state (T<sub>1</sub>) to the lowest singlet excited state (S<sub>1</sub>) by thermal activation to produce the delayed fluorescence. The EL processes in TADF molecules are showed in Fig. 2. Therefore, the 100% IQE could be realized based TADF OLEDs in theory and the typical transient decay curve exhibits two lifetime: one is prompt lifetime with ~ns magnitude and the other is delayed lifetime with ~µs, even ~ ms magnitude.

## 3. Advantages of exciplex and TADF materials as the host

From the discussion of exciplex formation process, and TADF materials design principle above, we can find that they have the natural advantages as the host to sensitize the dopant of fluorescent and phosphorescent emitters.



Fig. 2. The EL processes in TADF molecules. PF: prompt fluorescence; DF: delayed fluorescence; NR: non-radiative transition.

#### 3.1. Exciplex as the host

We could summarize the exciplex host conducts the advantages as follows:

First, the bipolar carriers transport characteristic. Exciplex host is the mixture of donor and acceptor materials, while the donor material is holes transport material and acceptor material is electrons transport material commonly. Thus, the bipolar carriers transport could be obtained, and more importantly, the mixed ratio also could be adjusted easily based on the characteristic of donor and acceptor to achieve the desired carriers transport and the balanced recombination of electrons and holes in emitting layer (EML).

Second, the broad excitons recombination zone. In traditional OLEDs, the excitons recombination zone is usually at the interface of holes transport layer/EML or EML/electrons transport layer due to the unipolarity of host. Even the excitons recombination zone would shift with the increased voltage, which is adverse to light-emitting. However, exciplex host has no the problems due to the bipolarity, and the excitons recombination zone would enlarge to the whole EML, which could reduce the excitons density and help to reduce the efficiency roll-off.

Third, the barrier-free charge injection from transport layer to EML. In generally, the holes transport layer and electrons transport materials are always the same as the donor and acceptor materials, respectively. Thereby, the interfacial barriers between transport layer and EML would be eliminated, and the electrons and holes could be injected into EML without energy barrier. So the turn-on voltage could be reduced efficiently, further to improve the device efficiency.

Fourth, the efficient RISC process of triplet excitons with TADF exciplex host contributes to improve emission performances of dopant. The efficient RISC process makes the triplet excitons could be utilized by Förster resonance energy transfer to dopant rather than Dexter process, the former is more efficient to improve the device efficiency and reduce efficiency roll-off, especially for traditional fluorescent dopant.

## 3.2. TADF materials as the host

We know that the design and synthesis of host materials in OLEDs is difficult because of the requirement of suitable HOMO/LUMO energy level, high triplet excitons energy and excellent carriers transport bipolarity. However, we suggest the TADF materials are the natural bipolarity materials due to the existence of donor and acceptor segments, which could transport the holes and electrons, respectively. The typical TADF materials of bis[4-(9,9-dimethyl-9,10-dihydroacridine)phenyl] sulfone (DMAC-DPS) had been proved the well bipolar [18].

Besides, the excellent TADF emission materials need high RISC and PL efficiency, which is also difficult to satisfy the two conditions simultaneously. While the high PL efficiency could be ignored when TADF materials as the host because the triplet excitons up-converted should be transferred to dopant rather than radiative transition, which reduces the design requirement of TADF molecules.

Finally, the energy transfer path with TADF materials as the host is different from the traditional host materials. The main energy transfer path from the traditional host to dopant is the Dexter energy transfer between triplet energy level ( $T_1$ ), while when TADF materials as the host, the Förster resonance energy transfer between singlet energy level ( $S_1$ ) dominate the key role. The very small  $\Delta E_{ST}$  in TADF materials host makes the triplet excitons up-convert rapidly to singlet excitons rather than direct Dexter energy transfer. So the primary energy transfer path in TADF materials host is the Förster energy transfer between  $S_1$ . Furthermore, the advantage of Förster energy transfer in TADF materials host could be maximized with traditional fluorescent dopant, which could break the 5% EQE upper limit. We know that the energy transfer between  $T_1$  from host to dopant is invalid because of the forbidden transition in traditional fluorescent dopants. Thereby, the triplet excitons up-conversion could enhance the singlet excitons ratio, which achieves high device EQE of > 5%, even exceeds 10% by the efficient Förster energy transfer process.

### 4. Applications of exciplex as the host in OLEDs

In this section, we utilize the various examples to clarify the practical application of exciplex host in OLEDs, including the phosphorescent, fluorescent and rare earth monochrome OLEDs and WOLEDs. When employing the exciplex as the host to design the device structure, some rules should be noticed: 1) the ratio of donor and acceptor should be optimized to make the exciplex conduct the well bipolarity due to the different materials characteristics. 2) the singlet and triplet excited state ( $S_1$  and  $T_1$ ) should be higher than dopant, and the overlap of exciplex PL spectra and dopant absorption spectra should be large, to ensure the efficient energy transfer. 3) it's better to adopt the donor and acceptor materials as the holes transport and electrons transport material, respectively, to eliminate the charge transport barriers. 4) the doping concentration is a very key factor, which should be optimized carefully.

## 4.1. Exciplex host in monochrome OLEDs

#### 4.1.1. In phosphorescent OLEDs

Kim group from Korea did much effort to utilize exciplex as the host sensitizing phosphorescent dopant since 2013 [19-23]. But the TADF characteristics of the exciplex host they employed had not been mentioned, so we could consider they adopted the exciplex without TADF as the host. The representative research results with high performance green, orange and blue phosphorescent OLEDs by employing exciplex as the host were all achieved by them. In green OLEDs with common Iridium(III)bis(2-phenylquinoline)acetylacetonate (Ir(ppy)<sub>2</sub>acac) as dopant, the 4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA) and bis-4,6-(3,5-di-3-pyridylphenyl)- 2-methylpyrimidine (B3PYMPM) were selected as donor and acceptor to form exciplex host to fabricate the device of ITO/TAPC (30 nm)/TCTA (10 nm)/TCTA: B3PYMPM: x wt% Ir(ppy)<sub>2</sub>acac (30 nm)/B3PYMPM (40 nm)/LiF (0.7 nm)/Al [21]. We can see that the corresponding holes and electrons transport layer materials are the same as donor and acceptor materials, which could eliminate the interface barrier to realize the barrier-free injection, further to reduce the turn-on voltage. Therefore, the turn-on could be decreased as low as to 2.4 V and the maximum EQE and power efficiency reach to 29.1% and 124 lm/W, respectively. More importantly, the EQE could keep as high as 27.8% at the luminance of  $10000 \text{ cd/m}^2$ . The author concluded the bipolar exciplex host, efficient energy transfer from exciplex host to dopant and low energy difference between the LUMO level of acceptor and HOMO level of donor were responsible for the high device performances. The orange OLEDs were achieved by doping green and red emitter of Ir(ppy)2(acac) and Iridium(III) (bis(2-(3,5-dimethylphenyl)quinoline acetylacetonate) (Ir(mphq)2acac), respectively, based on the same exciplex host mentioned above with the structure of ITO/TAPC (20 nm)/TCTA (10 nm)/TCTA: B3PYMPM: 8 wt % Ir(ppy)2acac: x wt% Ir(mphq)2acac (30 nm)/B3PYMPM (45 nm)/LiF (0.7 nm)/Al [22]. The low turn-on voltage of 2.4 V and high maximum EQE of 25% were obtained at the red emitter doping concentration of 0.3 wt%. The device also exhibited a small efficiency roll-off of 21% at 10000 cd/m<sup>2</sup>. The important light-emitting device of blue OLEDs with Iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C2']picolinate

(FIrpic) as dopant was also fabricated by high triplet energy exciplex host, which adopted m-bis(N-carbazolyl)benzene (mCP) and (1,3,5-triazine-2,4,6-triyl) tris(benzene-3,1-diyl) tris(diphenylphosphine oxide) (PO-T2T) as the donor and acceptor, respectively [23]. The blue OLEDs conducted the structure of ITO/mCP: 6% ReO<sub>3</sub> (45 nm)/mCP (15 nm)/mCP: PO-T2T: 10% FIrpic (30 nm)/PO-T2T (20 nm)/PO-T2T: 4% Rb<sub>2</sub>CO<sub>3</sub> (25 nm)/Al. The low driving voltages of 2.75 V, 3.29 V and 4.65 V at 100, 1000 and 10000 cd/m<sup>2</sup>, respectively, were realized and a



**Fig. 3.** The two kinds of different phosphorescent device structures and energy level of each layer. Device 1: exciplex host; Device 2: single host. Reproduced with permission from ref. 24.

high maximum EQE and power efficiency of 30.3% and 66  $\rm lm/W$  was demonstrated simultaneously.

In order to clarify the emission mechanism in depth of phosphorescent OLEDs with exciplex host. Kim group fabricated two kinds of device structures as follows: one with the exciplex forming host of TCTA: B3PYMPM (Device 1) and the other with a single host of 4,4'-N,N'-dicarbazole-biphenyl (CBP) (Device 2) [24]. The device structures are showed in Fig. 3 and the emission mechanisms were analyzed using the current density-voltage-luminance characteristics in diffusion current region, transient EL and capacitance-voltage measurements. The results clearly showed that excitons were predominantly generated by Langevin recombination in the exciplex host, in contrast to the trapassisted recombination on the emitter in the CBP host. Also, the trapped charge density with the exciplex host system was lower than that in the CBP host. These results indicated that the exciplex host boosts the recombination of the charge carriers in the host by Langevin recombination and boosts the light emission from the emitter through energy transfer from the host rather than by trap-assisted recombination, even in the high current region. Low charge density in the OLEDs with the exciplex host is also related to the low efficiency roll-off caused by reduced exciton polaron quenching.

Our group also did some researches on exciplex host to use the mCP as donor and 4,7-diphenyl-1,10-phenanthroline (Bphen), 1,3,5-tris(Nphenyl-benzimidazol-2-yl)benzene (TPBi) and PO-T2T as acceptor, respectively [25]. The three exciplexes all showed blue emission and the EQEs were below 3%, but they could also be employed as the host to sensitize phosphorescent emitter of bis(2-phenylbenxothiozolato-N,C2') iridium(III) (acetylacetonate) (Ir(bt)2acac). The EQE could reach 16.9% with mCP: PO-T2T as the exciplex host, which demonstrated the highly efficient energy transfer was more important than EL efficiency of exciplex to achieve high efficiency dopant emission in exciplex host system. In the exciplex system, the ratio of donor and acceptor in EML is another key factor to realize the charge balance. Yuan et al. fabricated high efficiency red OLEDs with maximum current efficiency, power efficiency and EQE of 33.7 cd/A, 37.7 lm/W and 20.3%, respectively, by adjusting the ratio of donor and acceptor [26]. Lee et al. also proposed the charge balance should be optimized based on the relative charge transport property of donor and acceptor materials for highly efficient OLEDs [27]. And they found that the device EL efficiency and lifetime would have a great differences by the precise optimization to the ratio of donor and acceptor among a large range with different exciplex host systems, which shown in Fig. 4. Therefore, the adjustable ratio of donor/acceptor to obtain the best charge balance is the maximum advantage of exciplex host compared to singlet host.

Tandem OLEDs are attracting significant interest because of their ability to realize high current efficiency and long operational lifetime. However, stacking multiple EL units in tandem OLEDs increases driving voltage and complicates fabrication process. Here, exciplex host could also be applied to tandem device due to its low driving voltage, which contributes to achieve low driving voltage and high power efficiency. Zhou et al. demonstrated low driving voltage tandem OLEDs via utilizing exciplex hosts in the EL units instead of conventional host materials [28]. The tandem device structure and EL efficiency are showed



**Fig. 4.** The effects of donor-acceptor mixing ratios on device performances in different exciplex hosts. (a) The device efficiencies and lifetimes. (b) Operating current densities and voltages at luminance of  $1000 \text{ cd/m}^2$ . (c) The current densities of HOD and EOD. HT: electron donor; HOD: hole only device; EOD: electron only device. Reproduced with permission from ref. 27.

in Fig. 5. The use of exciplex hosts reduces the charge injection barriers and the trapping of charges on guest molecules, resulting in the lower driving voltage.

There had also existed the mixed host by mixing holes transport materials and electrons transport materials before the exciplex host was provided. Song et al. studied the light emission mechanism of OLEDs with a mixed host EML by using an exciplex type mixed host of TCTA: TPBi and an exciplex-free type mixed host of CBP: TPBi [29]. By monitoring of the current density and luminance of the two type mixed host devices, they revealed that the light emission process of the exciplex type mixed host was dominated by energy transfer, while the light emission of the exciplex-free mixed host was controlled by charge trapping. The related emission mechanism was described in Fig. 6.

Except for the mixed structure exciplex host, the interfacial structure exciplex-forming could also be as the host to sensitize dopant [30,31]. To investigate the effect of interfacial exciplex formation, Seino et al. fabricated two types of blue phosphorescent OLEDs. The device structure was ITO/TAPC (30 - x nm)/TCTA (x nm) with x = 0 or 5 nm/BTPS: 11 wt% FIrpic (10 nm)/B3PyPB (50 nm)/Liq (1 nm)/Al [31]. The OLEDs with TCTA gave an power efficiency of 45.5 lm/W



Fig. 5. The structures and efficiencies curves of tandem devices. (a) Schematic structures of devices T-C-2 and T-E-2. (b) Luminance-voltage curves. Inset: current density-voltages curves. (c) Current efficiency-current density curves. (d) power efficiency-current density curves. Inset: normalized EL spectra. S-C-2 and S-E-2: single device based CBP host and exciplex host; T-C-1 and T-E-1: tandem device based CBP host and exciplex host, and Bphen: LiNH<sub>2</sub>/MoO<sub>3</sub> intermediate connectors; T-C-2 and T-E-2: tandem device based CBP host and exciplex host, and Bphen: LiNH<sub>2</sub>/HAT-CN intermediate connectors. Reproduced with permission from ref. 28.

with an driving voltage of 3.32 V at 100 cd/m<sup>2</sup>. While the device performances without TCTA achieved higher power efficiency of 50.1 lm/ W at 100 cd/m<sup>2</sup>, and with much lower driving voltage of 2.90 V than that in the device with TCTA. The OLEDs without TCTA showed much lower driving voltages despite the large hole injection barrier of 1.1 eV between TAPC and 5',5'''-sulfonyl-di-1,1':3',1"-terphenyl (BTPS). The OLEDs without TCTA gave a turn-on voltage of 2.50 V, which was almost equal to the energy difference between HOMO of di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexan (TAPC) and LUMO of BTPS, strongly suggesting the carrier recombination pathway via the exciplex formation between TAPC and BTPS. In other words, a barrier free holeelectron recombination mechanism at the interface between TAPC and BTPS was suggested, leading to the reduced driving voltage.

## 4.1.2. In fluorescent OLEDs

In generally, the emission of dopant in the host-guest doped system is from the host energy transfer (Förster and Dexter type) process and direct charge trapping recombination process, and all the processes are efficient for phosphorescent dopant due to the radiative transition of triplet excitons by itself. However, for traditional fluorescent dopant, the triplet excitons are invalid because of the forbidden transition. So how to break the 5% upper limit of EQE in traditional fluorescent OLEDs is an important issue. Here, exciplex host with TADF characteristics has the huge potential to achieve high efficiency traditional fluorescent emission. The triplet excitons up-conversion in TADF exciplex host could increase the singlet excitons ratio (> 25%) and improve the EQE of traditional fluorescent OLEDs. The energy transfer and emission processes in this system are showed in Fig. 7. The 75% triplet excitons produced on exciplex host up-convert to singlet excitons by efficient RISC and then reach to the singlet excited state of traditional fluorescent dopant for radiative transition by the efficient Förster energy transfer process. Dexter energy transfer and direct trapping recombination that outside of the path mentioned above are a kind of waste to triplet excitons and have no help in improving device



**Fig. 6.** The emission mechanism of mixed host devices. (a) Exciplex type mixed host of TCTA: TPBi device. (b) Exciplex free type mixed host of CBP: TPBi device. HTL: holes transport layer; ETL: electrons transport layer. Reproduced with permission from ref. 29.

efficiency. To ensure the efficient energy transfer process shown in the Fig. 7 for achieving high efficiency traditional fluorescent OLEDs, there are two key factors that need to be considered: First, most of the excitons should be formed on the exciplex host and the charge trapping by the fluorescent dopant should be avoided as much as possible. Second, the triplet excitons formed on the exciplex host should try to avoid reaching  $T_1$  energy level of the fluorescent dopant by Dexter energy transfer. That is, in this system, the processes of reaching the  $T_1$  energy level of the dopant by any means are disadvantageous in achieving the high efficiency traditional fluorescent OLEDs.

Liu et al. prepared the high efficiency green fluorescent OLEDs with two different host architecture devices of ITO/TAPC (40 nm)/TAPC: DPTPCz: 1 wt% C545T (30 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al and ITO/TAPC (40 nm)/mCP (5 nm)/DPTPCz: 1 wt% C545T (30 nm)/ TmPyPB (50 nm)/LiF (1 nm)/Al [32]. The former was the exciplex host



Fig. 7. The energy transfer and emission processes with exciplex host sensitizing traditional fluorescent dopant. PF: prompt fluorescence; DF: delayed fluorescence.



**Fig. 8.** The schematic diagrams of energy transfer mechanisms in two different host architecture devices and molecular structures. (a) In exciplex host system of TAPC: DPTPCz. (b) In common single host system of DPTPCz. (c) The molecular structures of organic compounds used in the paper. Reproduced with permission from ref. 32.

of TAPC: 3-(4,6-diphenyl-1,3,5-triazin-2-yl)-9-phenyl-9H-carba-zole (DPTPCz) and the latter was the common single host of DPTPCz. The green OLEDs with exciplex host showed a low turn-on voltage of 2.8 V as well as high maximum current efficiency, power efficiency and EQE of 44.0 cd/A, 46.1 lm/W and 14.5%, respectively, which was close to 100% triplet excitons harvesting and much higher than the single host device. These results demonstrated a simple approach for harvesting  $\approx$  100% triplet excitons in OLEDs based traditional fluorescent dopant through efficient energy transfer from exciplex host. Author also expounded the emission mechanism and made a comparison with common host, which exhibited in Fig. 8. Two critical requirements have to be satisfied: (a) using a TADF exciplex host with its HOMO and LUMO close to the fluorescent dopant to minimize charges trapping; (b) using an extremely low dopant concentration to minimize triplet-triplet energy transfer from the host to the dopant. So the highly efficient RISC and Förster energy transfer could ensure the efficient utilization of triplet excitons to achieving almost 100% IQE.

Almost at the same time, Kim group and our group reported the high efficiency 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-envl)-4H-pyran (DCJTB) emission exceeding 10% EQE with different exciplex host of TCTA: 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B4PYMPM) and TCTA: PO-T2T, respectively [33,34]. The device structures were very simple and as follows: ITO/TAPC (75 nm)/TCTA (10 nm)/TCTA: B4PYMPM: x wt% DCJTB (30 nm)/B4PYMPM (50 nm)/ LiF (0.7 nm)/Al, and ITO/MoO<sub>3</sub> (3 nm)/NPB (20 nm)/TCTA (8 nm)/ TCTA: 3P-T2T: x wt% DCJTB (15 nm)/3P-T2T (45 nm)/LiF (1 nm)/Al. The analysis of transient PL indicated the RISC of triplet excitons on exciplex host followed by the energy transfer to DCJTB play the crucial role of high efficiency. Furthermore, different from the phosphorescent dopant, the influence of doping concentration on device efficiency is very large with traditional fluorescent dopant, which results in the doping concentration need be controlled precisely. Besides, other highly efficient traditional fluorescent OLEDs with exciple host, including the structure of bilayer interface exciplex host sensitizing dopant also had been reported [35]. Thereby, the appearance of TADF exciplex host provided an



**Fig. 9.** The schematic illustration of the excited state processes of a TADF emitter doped in different host. (a) Schematic concept of combined inter- and intra-molecular charge transfer (CT) processes for fluorescence OLEDs. Processes are shown using arrows, with broken arrows representing non-radiative (NR) decay. The exciplex states are shown as energy bands to express the distribution of energy levels. Charge recombination in the exciplex host, ISC and RISC processed on the exciplex, and Förster energy transfer (ET) to the dopant increase the singlet ratio of the TADF dopant than 25%. The increased singlet population suppresses the triplet exciton annihilation reducing the efficiency at high current densities. (b) Recombination and emission in a conventional single host-TADF dopant system. The recombination and only 25% of singlet excitons are initially generated on the dopant. Reproduced with permission from ref. 36.

efficient way to obtain high efficiency traditional fluorescent OLEDs.

Except for the traditional fluorescent dopant, the TADF materials proposed recent years are also fluorescent materials. Moon et al. combined inter- and intra-molecular charge transfer processes by using an exciplex host and a TADF dopant for fabricating efficient fluorescent OLEDs (ITO/TAPC (x nm)/TCTA (10 nm)/TCTA: B3PYMPM: 7 wt% DACT-II (30 nm)/B3PYMPM (55 nm)/LiF (1 nm)/Al) [36]. TCTA and B3PYMPM were selected as an exciplex host with inter-molecular charge transfer process and 9-[4-(4,6-diphenyl-1,3,5-triazin-2-yl) phenyl]-N,N,N',N'-tetraphenyl-9H-carbazole-3,6-diamine (DACT-II) as a TADF dopant with intra-molecular charge transfer process, as a result of high efficiency with maximum EQE of 34.2%, current efficiency of 114 cd/A, power efficiency of 121.3 lm/W were achieved, along with low efficiency roll-off. The schematic illustration of the excited state processes of a TADF emitter doped in an exciplex host and in a single host is showed in Fig. 9. In the exciplex host, light emission mostly takes place via excitons formation on the host molecules as exciplex followed by energy transfer to the TADF dopant molecules rather than the trapassisted recombination in a single host due to smaller trap energy in the exciplex host than the single host. The RISC taking place in exciplex will increase the singlet excitons ratio larger than 25% owing to a longer range of energy transfer from singlet exciplexes to singlet excitons of the TADF dopant, compared with that of triplet exciplexes to dopant triplet excitons. In contrast, the recombination in single hosts is expected to take place mostly on TADF dopant molecules via trap-assisted recombination similar to phosphorescent doped OLEDs. This extra conversion from triplet exciplexes to singlet exciplexes has an effect to reduce the triplet density in the TADF molecules to reduce the efficiency roll-off compared to the single host systems. The similar device structure design with exciplex as the host and TADF materials as the dopant were also reported by other groups [37,38]. We also believe that the device performances could reach the level of phosphorescent OLEDs, even better when using the inter- and intra-molecular charge transfer processes.

#### 4.1.3. In rare earth OLEDs

The application of exciplex host on rare earth complex emitter was also researched first time by our group. We adopted the simple device structure with the exciplex of TCTA: Bphen as the host to sensitize the

#### Table 1

The summary of roll-off ratio in this work and	l other reports before base	d on the emission of Eu-com	plex. Reproduced	with permission fror	n ref. 39.
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EML structure	V <sub>on</sub> <sup>a</sup> [V]	EQE <sub>Max.</sub> b [%]	EQE <sub>100</sub> <sup>c</sup> [%]	$EQE_{max.} \sim EQE_{100}^{d}$ [%]	Ref.
TCTA:Bphen: 5 wt% Eu(DBM) <sub>3</sub> Phen	2.8	0.87	0.74	15	[39]
TCTA:Bphen: 10 wt% Eu(DBM) <sub>3</sub> Phen	2.9	2.12	1.86	12	[39]
TCTA:Bphen: 15 wt% Eu(DBM) <sub>3</sub> Phen	2.9	1.71	1.40	18	[39]
CBP:PBD: 5 wt% Eu(DBM) <sub>3</sub> Bphen	N/A	5.3	4.3	19	[40]
PVK:PBD: 1 wt% Eu(FTA) <sub>3</sub> Phen	8.1	4.28	~1.5	65	[41]
PFO-PBD: 4% Eu(DBM) <sub>3</sub> DBrPhen	12	1.45	1.1	24	[42]
PFO-PBD: 1% Eu(DBM) <sub>3</sub> DTPA-Phen	7.4	1.8	~0.9	50	[43]
TPD: 33% Eu(DBM)3BPhen	N/A	7.8	4.9	37	[44]
CBP: 1% Eu(TTA) <sub>3</sub> Tmphen	7	4.3	2.2	49	[45]
CBP: 8% Eu(DBM)3sbf	4	2.91	1.8	38	[46]
CBP: 10% Eu(TTA) <sub>3</sub> EFDPO	9	2.21	0.52	76	[47]

<sup>a</sup> Turn-on voltage.

<sup>b</sup> EQE at Maximum.

<sup>c</sup> EQE at 100 cd/m<sup>2</sup>.

<sup>d</sup> EQE roll-off ratio from maximum EQE to EQE at  $100 \text{ cd/m}^2$ .

rare earth europium complex of tris(dibenzoylmethane)mono(1,10phenanthroline)europium(III) (Eu(DBM)<sub>3</sub>Phen) with red emission [39]. The device structure was as follows: ITO/MoO<sub>3</sub> (3 nm)/TCTA (25 nm)/ TCTA: Bphen: x wt% Eu(DBM)<sub>3</sub>Phen (15 nm)/Bphen (40 nm)/LiF (1 nm)/Al. With the optimal doping concentration of 10 wt%, we achieved a low turn-on voltage of 2.9 V and high current efficiency, power efficiency and EQE values of 3.85 cd/A, 2.26 lm/W and 2.12%, respectively; more importantly, the roll-off ratio of EQE from maximum to  $100 \text{ cd/m}^2$  was only 12%. The roll-off ratios of other previous reports on Eu-complex are also listed in Table 1 for comparison, which demonstrate further the advantage of exciplex host to decrease the driving voltage. When changing the exciplex host to mCP: PO-T2T, the turn-on voltage decreased to 2.5 V and the maximum current efficiency, power efficiency and EQE reached 5.51 cd/A, 4.94 lm/W and 3.11%, respectively. Such low turn-on voltage, high efficiency and low efficiency rolloff could be attributed to barrier-free carrier injection, balanced carrier transport and recombination, and high energy transfer efficiency from the exciplex host to the Eu-complex.

#### 4.2. Exciplex host in WOLEDs

The application of exciplex host in WOLEDs also received many attentions due to the low driving voltage followed by high power efficiency, which was very important for WOLEDs to reduce the power consumption. The dopants in this section have no distinction, which could be fluorescent and phosphorescent dopant. And we pay the focus on the device structure to design WOLEDs with exciplex host.

The first high efficiency WOLEDs adopting exciplex as host published by Kim group [48]. They fabricated tandem WOLEDs (ITO/mCP: 4 wt% ReO<sub>3</sub> (x nm)/mCP (15 nm)/mCP: B3PYMPM: 10 wt% FIrpic (15 nm)/B3PYMPM (15 nm)/B3PYMPM: 4 wt% Rb<sub>2</sub>CO<sub>3</sub> (25 nm)/ Bphen: 23 wt% Rb<sub>2</sub>CO<sub>3</sub> (10 nm)/HATCN (y nm)/TAPC (20 nm)/TCTA (10 nm)/TCTA: B3PYMPM: 8 wt% Ir(ppy)<sub>2</sub>(tmd): 0.2 wt% Ir  $(mphmq)_{2}(tmd)$  (15 nm)/B3PYMPM (60 nm)/LiF (0.7 nm)/Al) by stacking blue and orange emission unit with exciplex host of mCP: B3PYMPM and TCTA: B3PYMPM, respectively. The exciplex host should have suitable excited state energy level to ensure the efficient energy transfer to dopant. The tandem WOLEDs achieved a high maximum EQE of 54.3% (PE of 63 lm/W), low efficiency roll-off with an EQE of 52.6% (PE of 52 lm/W) at 1000  $cd/m^2$ , and high color stability. In addition to the tandem structure, typical WOLEDs with single EML structure of ITO/MoO<sub>3</sub> (1 nm)/CDBP (45 nm)/CDBP: PO-T2T: 7.5 wt % 2CzPN: 0.6 wt % AnbCz (30 nm)/PO-T2T (45 nm)/LiF (1 nm)/Al were reported by Zheng group with 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl (CDBP): PO-T2T as exciplex host, 1,2-bis(carbazol-9-yl)-4,5-dicyanobenzene (2CzPN) of sky blue emitter and 2,6-di(9H-carbazol-9-yl) anthracene-9,10-dione (AnbCz) of orange-red emitter as dopants to realize white emission [49]. The highly simplified WOLEDs based on this concept achieved an extremely low turn-on voltage of 2.3 V, maximum current efficiency, power efficiency and EQE of 50.1 cd/A, 63.0 lm/W and 19.0%, respectively.

The exciplex in the WOLEDs mentioned above acts the role of pure host and the complete energy transfer occurs. Actually, compared to the application of exciplex as the host to sensitize dopants, a very simple single layer structure WOLEDs by combining the emission of blue exciplex host and orange dopant through the incomplete energy transfer could be achieved. Many researchers obtained the highly efficient WOLEDs with the simple device structure [50-52]. Zheng group employed (4-dimesitylboryl)phenyltriphenylamine (TPAPB): TPBi exciplex as blue emitter, and the host for orange dopant simultaneously to achieve the white emission, which conducted the structure of ITO/ TPAPB (30 nm)/TPAPB: TPBi: 0.5 wt% Ir(2-phq)<sub>3</sub> (30 nm)/TPBi (40 nm)/LiF (1 nm)/Al [50]. Thus, the device used merely three organic layers and three organic materials, which not only endowed the device with low operating voltages but also effectively reduced the production cost. The WOLEDs exhibited excellent efficiency performance with maximum EQE of 15.7%, current efficiency of 42.5 cd/A and power efficiency of 29.6 lm/W. Our group also fabricated kinds of highly efficiency WOLEDs with blue exciplex host of 3,3-di(9H-carbazol-9-yl) biphenyl (mCBP): PO-T2T by employing different orange dopants of traditional fluorescent, phosphorescent, TADF emitters [51]. The device structure designed and schematic diagram of incomplete energy transfer from blue exciplex to the orange dopant were showed in Fig. 10. The incomplete energy transfer between blue exciplex and orange dopant simplified the WOLEDs structure to only three organic



**Fig. 10.** The device structure and schematic diagram of incomplete energy transfer from blue exciplex to the orange phosphor/fluorophor. Left: domain I and II in blue dash dot and red dash rectangles indicate the doped areas of orange dopant, correspond to WOLEDs with two EML and one EML. Right: Jablonski diagram of incomplete energy transfer from exciplex to orange phosphor/fluorophor in the WOLEDs. F: fluorescence; DF: delayed fluorescence; ET: energy transfer; NR: non-radiative process; P: phosphorescence. Reproduced with permission from ref. 51.



**Fig. 11.** The device structures and performances of all-fluorescence and fluorescence/phosphorescence (F/P) hybrid WOLEDs. (a) Schematic of the optimized device structure, all-fluorescence WOLEDs with the EML of CDBP: PO-T2T: 0.3% TBRb; single-EML hybrid WOLEDs with CDBP: PO-T2T: 0.3% PO-01; tri-EML hybrid WOLEDs with CDBP: PO-T2T: 5% PO-01/CDBP: PO-T2T: 0.3% PO-01/CDBP: PO-T2T: 5% PO-01. (b) The current density and luminance versus the driving voltage characteristics. (c) The EQE and power efficiency versus luminance characteristics. A peak EQE of 20.8% and power efficiency of 75.4 lm/W for fluorescent white device, and 29.0% and 108.2 lm/W for hybrid white device. (d) EL spectra of the fabricated all-fluorescence WOLEDs; Inset: the photograph of WOLEDs at 20 mA/cm<sup>2</sup>. Reproduced with permission from ref. 54.

layers, along with low driving voltage and high efficiency, which showed promising prospect.

Ma group also did some efforts to employ exciplex host for WOLEDs, including ultrathin layer and multi-EML with sandwich structure [53,54]. By adopting an exciplex system as host for the blue emitter, and simply inserting an ultrathin nondoped layer of highly efficient orange emitter within the blue layer, WOLEDs with the structure of ITO/MoO<sub>3</sub> (10 nm)/TAPC: MoO<sub>3</sub> (10%, 50 nm)/TAPC (20 nm)/PO-01 (0.06 nm)/mCP: B3PYMPM: FIrpic (1: 1: 0.4, 10 nm)/B3PYMPM (15 nm)/B3PYMPM: Li<sub>2</sub>CO<sub>3</sub> (3%, 40 nm)/Li<sub>2</sub>CO<sub>3</sub> (1 nm)/Al achieved the low driving voltage, high efficiency and reduced efficiency roll-off successfully [53]. The maximum efficiencies reached 64.5 cd/A, 75.3 lm/W and 20.0% without using light out-coupling technique and remained 62.8 cd/A, 63.1 lm/W and 19.5% at the luminance of 1000 cd/ m<sup>2</sup>. Further, highly efficient all-fluorescence and fluorescence/phosphorescence (F/P) hybrid WOLEDs with low efficiency roll-off by designing exciplex host emissive architecture and precisely manipulating the excitons allocation were demonstrated in Fig. 11 [54]. The resulting complementary-color hybrid WOLEDs with sandwich structure realized the maximum EQE of 28.3% and power efficiency of 102.9 lm/W, and remain 26.9% and 73.5 lm/W at 500 cd/m<sup>2</sup> and yet as high as 25.8% and 63.5 lm/W at 1000 cd/m<sup>2</sup>, respectively, revealing very low efficiency roll-off.

The summary of fluorescent and phosphorescent monochrome OLEDs, and WOLEDs based on exciplex host are listed in Table 2. Based on the discussions of exciplex host mentioned above, we can see that the low turn-on voltage, high efficiency and small efficiency roll-off could be realized by employing exciplex as the host. The molecular structures of common donor and acceptor are listed in Fig. 12.

## 5. Application of TADF materials as the host in OLEDs

In the introduction, we present that the TADF emitters are considered as the third generation emission materials in OLEDs, however, which could also be acted as the host due to its natural advantages. So in this section, the applications of TADF materials as the host in OLEDs are discussed. When using TADF materials as the host to design OLED, the high PL radiative efficiency could be weaken because the singlet excitons that produced by RISC would be transferred to the dopant rather than radiative transition. Therefore, the high RISC efficiency and high energy transfer efficiency would be the main consideration when selecting the TADF materials as the host.

## 5.1. TADF materials as the host in monochrome OLEDs

## 5.1.1. In phosphorescent OLEDs

As we know, phosphorescent materials can harvest both singlet and triplet excitons to achieve 100% IOE. But the relatively short operational lifetime and the high cost owing to the costly emitter with a concentration about 10% in the EML limit the development of phosphorescent OLEDs. Besides, the serious efficiency roll-off at high current density is also a problem in phosphorescent OLEDs. While the short operational lifetime, high cost and serious efficiency roll-off in phosphorescent OLEDs could be solved with TADF materials as the host due to the utilization of triplet excitons through the RISC rather than the Dexter energy transfer to dopant [60-62]. So the concentration of phosphorescent dopant could reduce from 6 to 15 wt% in conventional phosphorescent OLEDs to 1-3 wt%, similar to the dopant concentration in fluorescent OLEDs. In another way, the singlet-triplet annihilation (STA) and triplet-triplet annihilation (TTA) which are the dominant origins of efficiency roll-off for phosphorescent OLEDs can be alleviated owing to the Förster energy transfer mechanism that suppresses intersystem crossing (ISC) process and decrease triplet excitons density in the rapid ISC-RISC circulations on TADF host. The schematic illustrations of energy transfer and emission process in phosphorescent OLEDs with TADF materials host were showed in Fig. 13.

Fukagawa et al. newly developed phosphorescent OLEDs employing only 1 wt% phosphorescent emitter exhibited an EQE of over 20% and a long operational lifetime of about 20 times that of an OLEDs consisting of a conventional host material and 1 wt% phosphorescent dopant [60]. In detail, the operational lifetime of LT50 (i.e. the time for the luminance to decay to 50% of the initial luminance) beyond 10000 h with initial luminance of 1000 cd/m<sup>2</sup> realized in the green phosphorescent OLEDs based on TADF material of 2-biphenyl-4,6-bis(12-phenylin-dolo [2,3-a]carbazol-11-yl)- 1,3,5-triazine (PIC-TRZ) as the host. Li et al. synthesized a TADF host material of 2,4-bisbiphenyl-6-(12-phenylindole[2,3-a]carbazole-11-yl)-1,3,5-triazine (BBPICT) and fabricated the red phosphorescent OLEDs with the structure of ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/BBPICT: x wt% Ir(mphmq)<sub>2</sub>(tmd) (30 nm)/Bphen (40 nm)/LiF (0.5 nm)/Al [61]. The devices displayed a maximum EQE of 20.9% and low efficiency roll-off of 1.7% at 1000 cd/ m<sup>2</sup>, and the operation lifetime of LT50 at an initial luminance of 1000 cd/m<sup>2</sup> was 1390 h. All the device performances were better than the CBP host device, which promised BBPICT a good choice as host of phosphorescent OLEDs to enhance efficiency, reduce efficiency roll-off and improve lifetime. Qi et al. also demonstrated a high efficiency and low efficiency roll-off orange phosphorescent OLEDs with the structure of ITO/MoO<sub>3</sub> (5 nm)/NPB (40 nm)/mCP (10 nm)/2CzPN: x wt% (tbt)<sub>2</sub>Ir (acac) (15 nm)/Bphen (40 nm)/Mg: Ag by using a TADF material of 2CzPN as host, which only required a low doping concentration (1 wt%) of (tbt)<sub>2</sub>Ir(acac) [62]. The device without light extraction optimization achieved the maximum power efficiency of 42.1 lm/W, current efficiency of 77.9 cd/A and EQE of 26.8%, respectively. Meanwhile, the EQE maintained 26.6% at  $1000 \text{ cd/m}^2$  and 25.8% at  $5000 \text{ cd/m}^2$ , respectively. According to the analyses, the efficiently utilized triplet excitons of 2CzPN via RISC of 2CzPN followed by host-guest Förster resonance energy transfer shown in Fig. 14 made significant contribution to the excellent device performance.

## 5.1.2. In fluorescent OLEDs

Similar to in the TADF exciplex host, the traditional fluorescent dopant in TADF materials host could also break the 5% EQE upper limit due to the efficient RISC and Förster energy transfer. The utilization of

#### Table 2

The summary of fluorescent and phosphorescent monochrome OLEDs, and WOLEDs based on exciplex host.

Exciplex host	Dopant	$V_{on}^{a}$	EQE <sub>Max.</sub> <sup>b</sup> [%]	EQE <sub>100</sub> <sup>c</sup> [%]	EQE1000 <sup>d</sup> [%]	Ref.
Exciplex host in phosphorescent OL	EDs					
ТСТА: ВЗРУМРМ	Ir(ppy) <sub>2</sub> acac	2.4	29.1		28.7	[21]
TCTA: B3PYMPM	Ir(ppy) <sub>2</sub> acac: Ir(mphq) <sub>2</sub> acac	2.4	25.0			[22]
mCP: PO-T2T	FIrpic	2.4	30.3		29.4	[23]
Tris-PCz: B4PyPPM	Ir(MDQ)2acac	2.3	20.3	19.9	17.3	[26]
TPAPB: TPBi	Ir(2-phq) <sub>3</sub>	2.9	18.5	17.0		[50]
CDBP: PO-T2T	Ir(ppy) <sub>2</sub> acac	2.5	28.6	26.2	23.3	[55]
CDBP: PO-T2T	Ir(MDQ) <sub>2</sub> acac	2.5	28.0	22.9	18.9	[55]
TPAF: B3PYMPM	Ir(ppy) <sub>2</sub> acac	2.15	20.1		19.5	[56]
TPAF: B3PYMPM	Ir(MDQ) <sub>2</sub> acac	2.35	19.2		11.2	[56]
mCP: B3PYMPM	FIrpic	3.0	29.5			[57]
NPB: PO-T2T	Ir(mphmq) <sub>2</sub> (tmd)	1.9	34.1		32.4	[58]
NPB: PO-T2T	Ir(MDQ) <sub>2</sub> (acac)	1.9	26.8		25.9	[58]
NPB: B3PYMPM	Ir(mphmq) <sub>2</sub> (tmd)	2.1	35.6		35.1	[58]
Exciplex host in fluorescent OLEDs						
Tris-PCz: B4PyPPM	DCJTB	2.3	9.3	7.3	5.1	[26]
TAPC: DPTPCz	C545T	2.8	14.5	12.0		[32]
TCTA: B4PYMPM	DCJTB	2.4	10.6			[33]
TCTA: 3P-T2T	DCJTB	2.17	10.15		10.03	[34]
ТСТА: ВЗРУМРМ	DACT-II		34.2		31.0	[36]
mCP: B3PyMPM	4CzIPN	3.0	29.6		27.8	[37]
CDBP: PO-T2T	2CzPN	2.3	19.5	8.9	3.5	[49]
CDBP: PO-T2T	4CzIPN	2.3	21.4	20.5	16.5	[49]
CDBP: PO-T2T	AnbCz	2.4	13.2	8.8	4.1	[49]
Exciplex host in WOLEDs						
CDBP: PO-T2T: 7.5 wt% 2CzPN: 0.6 w	t% AnbCz	2.3	19.0		5.6	[49]
TPAPB: TPBi: 0.5 wt% Ir(2-phq) <sub>3</sub>		3.2	15.7	14.0		[50]
mCBP: PO-T2T: 0.5 wt% Ir(bt) <sub>2</sub> (acac)		2.5	22.21		20.56	[51]
mCBP: PO-T2T: 0.4 wt% Rubrene		2.5	7.05		6.07	[51]
PO-01 (0.06 nm)/mCP: B3PYMPM: FIrpic (1:1: 0.4)		2.4	20.0		19.5	[53]
CDBP: PO-T2T: 0.3% TBRb		2.6	20.8			[54]
CDBP: PO-T2T: 0.3% PO-01		2.5	29.0		15.8	[54]
CDBP: PO-T2T: 5% PO-01/CDBP: PO-T2T: 0.3% PO-01/CDBP: PO-T2T: 5% PO-01		2.5	28.3		25.8	[54]
CDBP: PO-T2T: 0.1wt% Ir(ppy) <sub>2</sub> acac: 0.3wt% Ir(MDO) <sub>2</sub> acac		2.5	25.5	20.8	14.8	[55]
mCP: B4PyMPM: 15 wt% FIrpic: 0.2 wt% PO-01		2.5	28.1	24.0	21.5	[59]

<sup>a</sup> Turn-on voltage.

<sup>b</sup> Maximum EQE.

<sup>c</sup> EQE at  $100 \text{ cd/m}^2$ .

<sup>d</sup> EQE at  $1000 \text{ cd/m}^2$ .

triplet excitons produced on TADF materials through RISC could increase the singlet excitons ratio (> 25%) and further improve the EQE of traditional fluorescent OLEDs.

The first to employ TADF materials as the host to sensitize traditional fluorescent dopant came from Adachi group. Here they reported traditional fluorescence-based OLEDs that realized EQEs as high as 13.4-18% for blue, green, yellow and red emission, indicating that the exciton production efficiency reached nearly 100% [63]. They proposed a promising route for triplet harvesting by applying TADF materials as an assistant dopant in OLEDs, which shown in Fig. 15. Thus, the OLEDs is composed of a double-dopant system-that is, a wide energy gap host, a TADF-assistant dopant and a fluorescent emitter dopant-that leads to 100% IQE. In this system, triplet excitons created on an assistant TADF materials  $(T_1^A)$  by electrical excitation are up-converted to the  $S_1$  state of the TADF materials ( $S_1^A$ ), and all  $S_1^A$  excitons are transferred to the  $S_1$  state of a fluorescent emitter ( $S_1^E$ ) via a Förster energy transfer process, which results in efficient radiative decay from  $S_1^{\ E}$  of the fluorescent emitter. Therefore, the cascade energy transfer scheme from TADF assistant dopants to fluorescent emitter dopants will be promising device architecture for OLEDs with ultimate performance.

To further simplify the device structure, Zhang et al. adopted an alternate method by employing the TADF materials as the host directly instead of assistant dopant [64]. They utilized two similar TADF

materials of PIC-TRZ and 2,4-diphe-nyl-6-bis(12-phenylindolo)[2,3-a] carbazole-11-yl)-1,3,5-triazine (DIC-TRZ) as host and traditional fluorescent material of 3,11-Diphenylamino-7,14-diphenylacenaphtho [1,2-k]fluoranthene (DDAF) as dopant shown in Fig. 16 to form the EML of PIC-TRZ: 1 wt% DDAF and DIC-TRZ: 1 wt% DDAF, respectively. PIC-TRZ is the first reported pure aromatic TADF compounds with a  $\Delta E_{ST}$  of 0.11 eV, while DIC-TRZ has a smaller  $\Delta E_{ST}$  of 0.06eV. But DIC-TRZ shows lower PL efficiency than PIC-TRZ in a toluene solution. As a result, the EL performance of the devices based DIC-TRZ host (Current efficiency: 36.4 cd/A; EQE: 11.7%) are better than the OLEDs based PIC-TRZ host (Current efficiency: 12.7 cd/A; EQE: 4.5%), which indicate the highly efficient RISC followed by Förster energy transfer rather than the PL efficiency plays the more important role in TADF materials host. The energy transfer and light emission processes they proposed are also described schematically in Fig. 16. Wang et al. used the typical TADF material of (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl) isophthalo-nitrile (4CzIPN) as the host and traditional fluorescent material of N,N'-Di(n-butyl)-2,9-difluoroquinacridone (C4-DFQA) as the dopant to construct OLEDs of ITO/NPB (35 nm)/mCP (5 nm)/4CzIPN: 0.5 wt% C4-DFQA (30 nm)/BCP (5 nm)/Bepp2 (40 nm)/LiF (0.5 nm)/Al [65]. By rapid RISC and efficient Förster energy transfer processes, the maximum values of EL performance could reach 13.5% of EQE and 53.4 lm/W of power efficiency, meantime the efficiency roll-off also had an



Fig. 12. The molecular structures of common donor and acceptor.



**Fig. 13.** The schematic illustration of energy transfer process and EML. (a) Energy transfer process from TADF material to phosphorescent emitter dopant. (b) EML in phosphorescent OLEDs with TADF host. (c) EML in phosphorescent OLEDs with conventional host. Reproduced with permission from ref. 60.



**Fig. 14.** The schematic diagram of emission process in phosphorescent OLEDs based on the EML of 2CzPN: (tbt)<sub>2</sub>Ir(acac) with a low dopant concentration of 1 wt%. Reproduced with permission from ref. 62.

obvious improvement.

Our group also fabricated the traditional fluorescent and phosphorescent OLEDs based 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-10-(2-benzothiazolyl)quinolizine-[9,9a,1gh]coumarin (C545T) and tris (2-phenylpyridinato) iridium(III) (Ir(ppy)<sub>3</sub>), respectively, with the structure of ITO/MOO<sub>3</sub> (3 nm)/mCP (25 nm)/DMAC-



**Fig. 15.** The energy transfer mechanism. (a) Schematic illustration of proposed energy transfer mechanism in the host matrix: assistant dopant: emitter dopant under electrical excitation and chemical structures of the assistant dopants used in this study. (b-e) Fluorescence spectra of host: assistant dopant co-deposited film (upper), and absorption (dashed line) and fluorescence (solid line) spectra of emitter dopant in solution  $(10^{-5} \text{ mol/L} \text{ in CH}_2\text{Cl}_2)$  (bottom). Rather large Förster transfer radii of ~2.2, ~7.3, ~6.9 and ~10 nm were estimated for blue, green, yellow and red EML matrices based on the spectral overlap between the absorption spectrum of the acceptor and the PL spectrum of the donor, suggesting that efficient Förster energy transfer (FRET) is possible. Reproduced with permission from ref. 63.



Fig. 16. The molecular structures of DIC-TRZ, PIC-TRZ and DDAF, and schematic diagram of energy transfer and light emission processes with TADF molecules sensitizing fluorescent dopant. PF: prompt fluorescence; DF: delayed fluorescence; ET: energy transfer. Reproduced with permission from ref. 64.

DPS: x% C545T or Ir(ppy)<sub>3</sub> (15 nm)/PO-T2T (45 nm)/LiF (1 nm)/Al, by utilizing DMAC-DPS as the universal host, which is a kind of highly efficient TADF material with blue emission [66]. As a result, The fluorescent OLEDs based C545T as the dopant with 1.5% concentration achieved almost the best performance under a luminance of 1000 cd/ $m^2$  with a current efficiency, power efficiency, and EQE of 31.8 cd/A,

25.0 lm/W, and 9.26%, respectively; meanwhile, the EQE roll-off ratio from maximum to the EQE at 1000 cd/m<sup>2</sup> was just ~1%. The utilization of triplet excitons through up-conversion and efficient energy transfer were responsible for the high efficiency. The phosphorescent OLEDs with Ir(ppy)<sub>3</sub> as the dopant with 4.0% concentration realized a very low roll-off at high luminance while earning a high efficiency of 64.3 cd/A, 62.4 lm/W, and 18.5%, respectively. The EQE roll-off ratio from maximum to the EQE at 1000 cd/m<sup>2</sup> was just ~3.5%, while the ratio was ~25% from maximum EQE to EQE at 10000 cd/m<sup>2</sup>. The barrier-free injection, balanced transport and recombination, wide carrier recombination zone, and host triplet excitons up-conversion are the reasons for the low efficiency roll-off with the fluorescent and phosphorescent OLEDs. We believe that the TADF materials still have more potential in the role of host.

## 5.2. TADF materials as the host in WOLEDs

In generally, the white light-emitting are composed of complementary colors based blue and orange or three primary colors based blue, green and red, even four colors with blue, green, orange and red. But no matter how many colors to form white emission, the blue emission is necessary, which means the blue material is essential in WOLEDs. So in this section of TADF materials host applied to WOLEDs, the blue TADF materials play the key role to constitute WOLEDs, besides the host materials should conduct higher energy to ensure the efficient energy transfer to low energy dopant.

The most extensive blue TADF material is DMAC-DPS based 9,10dihydroacridine/diphenylsulphone derivative, whose blue OLEDs based DMAC-DPS offered maximum EQE of 19.5% and reduced efficiency roll-off characteristics at high luminance [7]. So many researchers constructed WOLEDs based on this blue TADF material of DMAC-DPS as host. Duan group demonstrated highly efficient single EML structure (ITO/HATCN (5 nm)/NPB (30 nm)/TCTA (10 nm)/mCP (10 nm)/ DMAC-DPS: x wt% PO-01 (30 nm)/DPEPO (10 nm)/Bphen (30 nm)/LiF (0.5 nm)/Al) hybrid WOLEDs based complementary colors with low roll-off and good color stability utilizing DMAC-DPS as host and blue emitter simultaneously [20]. The simplified WOLEDs achieved the highest EQE of 20.8% and power efficiency of 51.2 lm/W with Commission Internationale de l'Eclairage (CIE) coordinates of (0.398, 0.456) at a luminance of  $500 \text{ cd/m}^2$ . The device EQE only slightly dropped to 19.6% at a practical luminance of  $1000 \text{ cd/m}^2$  with a power efficiency of 38.7 lm/W. Duan group also achieved the high color stability and high color rendering index (CRI) single EML structure hybrid WOLEDs based three colors by employing the same TADF materials host of DMAC-DPS: ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/DMAC-DPS: 0.2 wt% Ir(ppy)2acac: 0.2 wt Ir(mphmq)2tmd (30 nm)/DPEPO (12 nm)/Bphen (30 nm)/LiF (5 nm)/Al [67]. The optimized WOLEDs exhibited the maximum EQE of 20.2% with the CRI of 85, the CIE coordinates of (0.360, 0.390) and small  $\Delta$ CIE of (0.012, 0.003). Even at the luminance of  $1000 \text{ cd/m}^2$ , the EQE just slightly decreased to 19.4%, indicating a low efficiency roll-off. The reason was that the RISC process of the TADF host materials enhances the Förster energy transfer in the EML, decreasing the triplet density under high current and thus alleviating the triplet deactivation process. Our group demonstrated highly efficient and color stable single EML structure (ITO/MoO<sub>3</sub> (3 nm)/TCTA (20 nm)/DMAC-DPS: x wt% rubrene (15 nm)/Bphen (40 nm)/LiF (1 nm)/Al) fluorescent WOLEDs using DMAC-DPS as host and traditional orange fluorescent material of rubrene as dopant [68]. At a low dopant concentration of 0.6 wt%, we achieved the efficient white emission with maximum current efficiency, power efficiency and EQE of 20.2 cd/A, 15.9 lm/W and 7.48%, respectively. Besides, the CIE coordinates were almost the same with the increased voltage, which shifted from (0.359, 0.439) to (0.358, 0.430) as the voltage rose from 5 V to 8 V. Song et al. developed fluorescent WOLEDs by co-doping DMAC-DPS and yellow emitters in a single EML (ITO/PEDOT: PSS (60 nm)/TAPC (10 nm)/TCTA (10 nm)/mCP (10 nm)/DPEPO: 50 wt%

DMAC-DPS: x wt% TBRb (25 nm)/TSPO1 (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al) [69]. DMAC-DPS in this EML acted the roles of fluorescent host and blue emitter, while the high EQE of 15.5% was achieved. Ma group presented a universal approach to high efficiency all fluorescent WOLEDs with extremely low efficiency roll-off using DMAC-DPS doped conventional fluorescent emitter of TBRb [70]. Using DMAC-DPS as a host, the resulting WOLEDs (ITO/TAPC: 20% MoO<sub>3</sub>/TAPC/mCP/ DMAC-DPS: x% TBRb/DPEPO/BmPyPB: 3% Li<sub>2</sub>CO<sub>3</sub>/Li<sub>2</sub>CO<sub>3</sub>/Al) exhibited the maximum power efficiency, current efficiency and EQE of 48.0 lm/W, 45.1 cd/A and 14.0%, respectively. At a practical brightness of  $1000 \text{ cd/m}^2$ , the device remain 29.3 lm/W, 42.0 cd/A and 13.0%. respectively, with CIE coordinates of (0.37, 0.48), indicating low efficiency roll-off. In addition to being utilized as the host, DMAC-DPS was also employed as the assistant dopant for the fluorescent orange emitter. The resulting WOLEDs (ITO/TAPC: 20% MoO<sub>3</sub>/TAPC/mCP/ DPEPO: DMAC-DPS: x% TBRb/DPEPO/BmPyPB: 3% Li<sub>2</sub>CO<sub>3</sub>/Li<sub>2</sub>CO<sub>3</sub>/ Al) showed excellent EL performances with the maximum power efficiency, current efficiency and EQE of 51.6 lm/W, 44.4 cd/A and 14.6%, respectively. Ma group also demonstrated another high performance WOLEDs based traditional fluorescent dopant by strategic management of singlet and triplet excitons within an efficient emissive zone, and the device structure was as follows: (ITO/MoO<sub>3</sub> (10 nm)/TAPC: 15.0 wt % MoO3 (50 nm)/TAPC (20 nm)/CzSi (5 nm)/DMAC-DPS: 0.5 wt % DBP (5 nm)/DMAC-DPS: 1.0 wt % DBP: 0.5 wt % TTPA (10 nm)/DMAC-DPS: 0.2 wt % TTPA (6 nm)/BmPyPB (10 nm)/BmPyPB: 3.0 wt % Li<sub>2</sub>CO<sub>3</sub> (45 nm)/Li<sub>2</sub>CO<sub>3</sub> (1 nm)/Al) [71]. This design consists of two separated red/green sub-EMLs with ultralow doping concentration and a sandwiched sub-EML doped with red and green fluorescent dyes at a relatively high concentration, which can harness all electrogenerated excitons and reduce the energy loss to the utmost extent. Accordingly, the resulting WOLEDs realized the EQE of 18.2% with a maximum power efficiency of 44.6 lm/W. At the practical luminance of  $1000 \text{ cd/m}^2$  for the lighting source, the EOE still remained as high as 16.2% with a CRI of 82 and stable color spectra. Qi et al. reported the hybrid WOLEDs with high color stability and efficiency by inserting an ultrathin nondoped orange EML between heavily doped blue EMLs based DMAC-DPS and the device was as follows: ITO/MoO3 (10 nm)/TAPC (40 nm)/mCP (10 nm)/DPEPO: 50 wt% DMAC-DPS (9 nm)/(tbt)<sub>2</sub>Ir(acac) (0.1 nm)/ DPEPO: 50 wt% DMAC-DPS (6 nm)/Bphen (40 nm)/Mg: Ag) [72]. As a result, a slight CIE coordinates variation of (0.008, 0.003) at a practical luminance range from 1000 to 10000  $cd/m^2$ , and the maximum power efficiency of 45.8 lm/W, EQE of 15.7% and EQE above 12% at 1000 cd/ m<sup>2</sup> had been obtained.

The energy transfer and emission process mechanism diagram of the WOLEDs with blue TADF materials as host are showed in Fig. 17. The key of design concept of DMAC-DPS as the host is the utilization of precise management of generated excitons and the incomplete energy transfer from DMAC-DPS molecules to fluorescent emitters. The high EL efficiency and low efficiency roll-off can be assigned to the enhanced Förster energy transfer, wide charge recombination zone, as well as the bipolar charge transporting ability of DMAC-DPS.



Fig. 17. The energy transfer and emission process mechanism diagram of the WOLEDs with blue TADF materials as host.



Fig. 18. The molecular structures of mSOAD and  $Ir(pq)_2acac$ , and device structure of non-doped WOLEDs. Reproduced with permission from ref. 75.

Very recently, our group newly synthesized a kind of blue TADF emitter of bis(3-(9,9-dimethyl-9,10-dihydroacridine)phenyl)sulfone (mSOAD) shown in Fig. 18 based zig-zag acridine/sulfone derivative [73]. Highly efficient WOLEDs with the blue TADF emitter as the host and iridium(III) bis(2-phenylquinoline) acetylacetonate (Ir(pq)<sub>2</sub>acac) as the dopant (ITO/MoO<sub>3</sub> (3 nm)/mCP (25 nm)/mSOAD: x wt% Ir (pq)<sub>2</sub>acac (20 nm)/DPEPO (5 nm)/TPBi (40 nm)/LiF (1 nm)/Al), were realized through the efficient management for excitons [74]. And all the WOLEDs with different dopant concentrations exhibited ultra-high color stability with the enhanced operation voltages, along with high maximum current efficiencies, power efficiencies and EQEs of 28.2-32.0 cd/A, 26.3-30.5 lm/W and 12.2-17.4%, respectively. Further, we utilized a simple method instead of host-guest doped system by employing an ultra-thin red phosphorescent emitter of Ir(pq)2acac into mSOAD to construct non-doped WOLEDs, which shown in Fig. 18 [75]. By the optimization of different locations and quantities of the ultra-



Fig. 19. The molecular structures of common TADF materials using as the host.

thin  $Ir(pq)_{2}acac$  emitter, the non-doped WOLEDs with superior efficiency and color stability were finally obtained. The maximum current efficiency, power efficiency and EQE of 31.9 cd/A, 30.4 lm/W and 17.3%, respectively, were achieved. Meantime, the CIE coordinates with a high color stability of (0.469 ± 0.008, 0.382 ± 0.004) from 4 V to 8 V were realized simultaneously. The high energy transfer efficiency and efficient confinement to carrier and excitons are the main reasons for the excellent device performance.

The summary of all kinds of OLEDs based TADF materials as the host are listed in Table 3. The molecular structures of common TADF materials using as host are listed in Fig. 19. Similar to the OLEDs based exciplex host, the low turn-on voltage, high efficiency and reduced

#### Table 3

The summary of fluorescent and phosphorescent monochrome OLEDs, and WOLEDs based on TADF materials as the host.

TADF materials host	Dopant	Von <sup>a</sup>	EQE <sub>Max.</sub> <sup>b</sup> [%]	EQE <sub>1000</sub> <sup>c</sup> [%]	Ref.
TADF materials host in phosphorescent OLEDs					
DMAC-DPS	PO-01	2.94	23.1	22.8	[18]
PIC-TRZ	Ir(mppy) <sub>3</sub>			20.3	[ <mark>60</mark> ]
BBPICT	Ir(mphmq) <sub>2</sub> tmd	2.6	20.9	19.7	[ <mark>61</mark> ]
BBPICT	Ir(ppy) <sub>3</sub>	2.6	19.4	18.1	[ <mark>61</mark> ]
2CzPN	(tbt) <sub>2</sub> Ir(acac)	4.6	26.8	26.6	[62]
DMAC-DPS	Ir(ppy) <sub>2</sub> acac		19.5		[67]
DMAC-DPS	Ir(mphmq) <sub>2</sub> tmd		22.4		[67]
mSOAD	Ir(pq) <sub>2</sub> acac	2.9	20.3	10.8	[74]
DCzIPN	PO-01	2.0	24.9		[76]
TADF materials host in fluorescent OLEDs					
DPEPO: 15 wt% ACRSA	TBPe	4.7	13.4	8.7	[63]
mCP: 50 wt% ACRXTN	TTPA	3.0	15.8	11.7	[63]
mCBP: 25 wt% PXZ-TRZ	TBRb	3.2	18.0	17.2	[63]
CBP: 15 wt% tri-PXZ-TRZ	DBP	3.0	17.5	10.9	[63]
DIC-TRZ	DDAF	2.5	12.2	5.5	[64]
4CzIPN	C4-DFQA	2.7	13.5	12.6	[65]
4CzIPN	C4-TCF3QA	2.8	14.6	13.7	[65]
DMAC-DPS	C545T	2.3	9.35	9.26	[66]
TADF materials host in WOLEDs					
DMAC-DPS: 0.8 wt% PO-01		3.06	20.8	19.6	[18]
DMAC-DPS: 0.2 wt% Ir(ppy) <sub>2</sub> acac: 0.2 wt% Ir(mphmq) <sub>2</sub> tmd		3.4	20.2	19.4	[67]
DMAC-DPS: 0.6 wt% rubrene		2.48	7.48	7.31	[68]
DPEPO: DMAC-DPS: 0.05 wt% TBRb			15.5	13.3	[69]
DMAC-DPS: 0.2% TBRb		2.8	14.0	13.0	[70]
DPEPO: DMAC-DPS: 0.2% TBRb		2.8	14.6	11.9	[70]
DMAC-DPS: 0.5 wt% DBP/DMAC-DPS: 1.0 wt% DBP: 0.5 wt% TTPA/DMAC-DPS: 0.2 wt% TTPA		2.8	18.2	16.2	[71]
DPEPO: DMAC-DPS/(tbt) <sub>2</sub> Ir(acac) (0.1 nm)/DPEPO: DMAC-DPS		3.1	15.7	12.1	[72]
mSOAD: $0.8 \text{ wt}\% \text{ Ir}(pq)_2 \text{ acac}$		2.8	16.2	8.7	[74]
mSOAD/~1 nm Ir(pq) <sub>2</sub> acac/mSOAD/~1 nm Ir(pq) <sub>2</sub> acac/mSOAD/~1 nm Ir(pq) <sub>2</sub> acac/mSOAD		2.7	17.3	11.5	[75]

<sup>a</sup> Turn-on voltage.

<sup>b</sup> Maximum EQE.

<sup>c</sup> EQE at  $1000 \text{ cd/m}^2$ .

efficiency roll-off could be also achieved in the OLEDs by utilizing the TADF materials as the host. The efficient utilization of triplet excitons through RISC process is the source of high OLEDs efficiency. The reduced efficiency roll-off under high luminance is mainly from two aspects: one is the host carrier transport bipolarity, which enlarges the excitons recombination zone, decreases polarons and excitons density, and finally contributes to reduce the TTA and TPA. The other is the efficient triplet excitons RISC followed by Förster resonance energy transfer from  $S_1$  of exciplex or TADF materials host to  $S_1$  of dopant. The RISC and long-range energy transfer way also conduce to reduce the efficiency roll-off.

### 6. Conclusion and outlook

Host materials occupy the very important role in OLEDs because almost all the highly efficiency OLEDs structure adopting host-guest doped system. In this review, we first introduce the inter-molecular charge transfer of exciplex and intra-molecular charge transfer of TADF materials. Then the natural advantages of exciplex and TADF materials as the host are summarized systematically. Finally, the practical applications of exciplex and TADF materials in monochrome OLEDs and WOLEDs are exhibited though other reports and our own works.

Exciplex host could simplify the devices structure and organic materials number at the greatest extent due to the holes and electrons transport layer materials are the same as the donor and acceptor materials, respectively. Meantime, the interfacial barriers could be eliminated to reduce turn-on voltage and improve power efficiency. The application of TADF materials as the host points the new design direction of TADF molecules, which conducts high RISC efficiency and energy transfer efficiency without high PL transition efficiency. So the high PL efficiency could be ignored when TADF materials as the host because that the triplet excitons up-converted would be transferred to dopant rather than direct radiative transition, which could lower the design requirement of TADF molecular. TADF materials host could also reduce the dopant concentration and improve lifetime to some degree in phosphorescent OLEDs. We also consider the exciplex and TADF materials as the host would act more crucial role in WOLEDs, because the low driving would result in high power efficiency, which is a more important factor in WOLEDs. Even so, some challenges with exciplex and TADF materials as the host need to be paid attention.

In current stage, the highly efficient blue exciplex and TADF materials are also short, especially as the host, which require higher energy in order to sensitize the dopant. The higher energy exciplex and TADF materials as the host to sensitize blue dopant face huge challenge. In other words, the highly efficient blue OLEDs is still an issue even the appearance of charge transfer host.

Exciplex and TADF materials as the host have exhibited huge potential in phosphorescent and TADF dopant, which could achieve high EQE of 20–30%. However, the device efficiency of traditional fluorescent dopant in exciplex host or TADF materials host is not so high and the efficiency is also dependent largely on the doped concentration compared to phosphorescent and TADF OLEDs. So highly efficient and concentration insensitive traditional fluorescent dopant in exciplex host or TADF materials host is an important and challenging issue.

Although the efficiency roll-off could be reduced by employing exciplex or TADF materials as the host, but not all the charge transfer host OLEDs could achieve the small efficiency roll-off. We consider the efficiency roll-off is a complex problem, which need to be explored further. Meantime, the stability of OLEDs with exciplex or TADF materials as the host is few reported, which should be researched systematically to accelerate the practical application of charge transfer host.

Finally, we review the application of recent developed new-type charge transfer host of exciplex and TADF materials in OLEDs. Although there exist some challenges, but the obvious advantages indicate its promising prospect as the host, and we also believe the exciplex and TADF materials as the host would become more and more important in OLEDs and may also promote the lighting industrialization of WOLEDs.

### Author contributions

Ziqi Wang (631138685@qq.com) wrote the sections of exciplex host. Chao Wang (alvin.wangchao@huawei.com) wrote the sections of TADF materials as the host. Heng Zhang and Zemei Liu helped to organize the figures, tables and references. Bo Zhao and Wenlian Li guided the manuscript writing and mechanism discussions. All the authors reviewed the manuscript.

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