

The recent progress and state-of-art applications for thermally activated delayed fluorescence (TADF)

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Abstract. Thermally activated delayed fluorescence (TADF) is regarded as the new generation of light-emitting materials in organic light-emitting diode after fluorescent materials and phosphorescent materials. Its high Internal Quantum Efficiency (IQE) and lower cost have attracted a lot of attention, which is a hot field of research of OLEDs for the future. This paper will summarize the achievements of TADF in research. Firstly, the article introduced the background of TADF and demonstrated the mechanism of TADF briefly. Subsequently, the article focused on the progress of TADF in red, green and blue light. Afterwards, the review discussed the limitations and future outlooks of TADF and finally drew a conclusion. These results shed light on guiding future studies focusing on TADF and lay a foundation for subsequent studies.

Keywords: TADF, Organic Light-Emitting Diode, IQE, RISC.

1. Introduction

Organic light-emitting diode (OLED) has been recognized as one of the most promising technologies for future displays, which is another light source revolution after incandescent lamps, fluorescent lamps, LCD, and LEDs [1, 2]. Its simple preparation process, low working voltage, rich material sources, high efficiency, low power, rich color and surface light source, ultra-thin, flexibility, without Hg and many other excellent characteristics has attracted widespread attention from the global display and lighting industry [1-6].

In the selection of luminescent materials in OLEDs, TADF materials is very popular because of its 100% exciton harvesting. Compared to the traditional phosphorescent materials, TADF has more stable performance, avoids the usage of expensive heavy metals, and reduces production costs. The phenomenon of thermally activated fluorescence was first discovered in 1961. Parker and Hatchard used a high-sensitivity spectrophosphorimeter recording the phosphorescence and delayed fluorescence emission in eosin in glycerol and ethanol [7]. In 1996, Berberan found the TADF mechanism in C70 can be discovered under appropriate conditions and pointed that it will be feasible only for molecules with small ΔE_{ST} [8]. A year later, Salazar also found the TADF in C60 with a higher singlet-triplet energy gap than C70 [9]. Adachi et al. designed the first pure aromatic compound PIC-TRZ [10], which also had the characteristics of TADF. In addition, it demonstrated a high External Quantum Efficiency (EQE) of 5.3% at lower current density compared to a conventional fluorescent material with EQE of 2%. Among them, the green OLEDs (doped 4CzIPN) achieved a very high EQE of 19.3% [11]. Then in 2015, Fujita et al. reported carbazole dendrimers with a triphenyl-s-triazine core, which are the first solution-processable, non-doped, high-molecular-weight TADF materials [12].

At present, the luminous color of the reported small molecule TADF material can almost cover the entire visible light spectrum, the device efficiency has exceeded 35% [13]. Although the small molecule has plenty of advantages, most of small molecules are used as dopants within a host material. Due to its fabricated technique by vacuum deposition, it is difficult to obtain large-scale of OLEDs devices and it is very expensive. In contrast, the polymeric materials are non-doped, more stable and can be fabricated by solution-process, which reduce sharply the cost of production. However, polymers have a wide molecular-weight distribution, low solubility and now a very low EQE compared to the small molecules [12].

Contemporarily, scholars designed a lot of TADF materials. The high-performance TADF material solves the problems of low efficiency, high cost and instability of traditional fluorescent and phosphorescent devices. The way to further improve their EQE and ameliorate the stability is a very important research field for TADF materials. This paper focused on the recent progress of TADF materials. The rest part of the paper is organized as follows. The mechanisms of TADF materials and working principle will be introduced and summarized in the Sec. 2. Afterwards, the Sec. 3 summarized the important achievements in state-of-art TADF research. Subsequently, the limitations and outlook in the future are discussed accordingly. Eventually, the summary of the paper is presented in Sec. 5.

2. TADF Mechanism

Theoretically, the IQE of TTA is only 62.5% [14], while the TADF has a higher IQE which can achieve nearly 100% compared to the TTA. TADF emitting light has two mechanisms: prompt fluorescence (PF) and delayed fluorescence (DF). Specifically, as for the PF mechanism, singlet excitons decay rapidly from S_1 to S_0 and emit fluorescence with a nanosecond level. In DF mechanism, triplet excitons convert from T_1 to S_1 by RISC and then decay promptly from S_1 to S_0 with a microsecond level lifetime.

In photoluminescence process, TADF materials absorb photons and then excite a ground level jump to form singlet excitons. Part of singlet excitons decay promptly to S_0 by radiative process or non-radiative process. Most of them transition to triplet excitons by Intersystem Crossing (ISC). Triplet excitons can up-convert into S_1 by RISC and then emit delayed fluorescence (seen from Fig. 1a). In Electroluminescence process [15,16], firstly electrons and holes recombine and produce singlet excitons and triplet excitons (the ratio of the two is 1:3). Secondly excitons transition from highly excited state to low excited state via vibrational relaxation (VR) and internal conversion (IC). Triplet excitons up-convert from T_1 into S_1 . Then these singlet excitons, forming via electrical excitation or conversion from T_1 , decay to S_0 (shown in Fig. 1b).

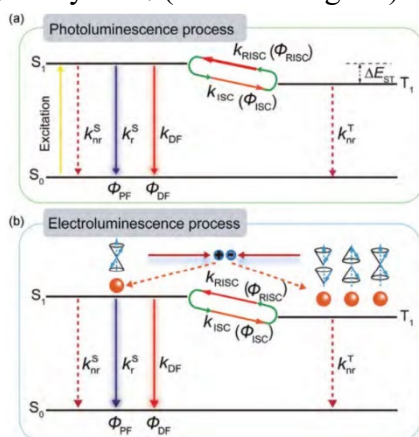


Figure 1. Photoluminescence process(a) and Electroluminescence process(b) [16].

External quantum efficiency is a very important parameter of OLEDs device and a higher Φ_{RISC} can improve it. EQE can be expressed as follows [10]:

$$EQE = \eta_{in}\eta_{out} = (\eta_r(S_1)\eta_f + [\eta_r(S_1)\Phi_{ISC}\Phi_{RISC} + \eta_r(T_1)\Phi_{RISC}])\gamma\eta_{out} \quad (1)$$

In this equation, η_{int} , η_{out} , $\eta_r(S_1)$, $\eta_r(T_1)$, η_f , γ is internal quantum efficiency, optical external coupling efficiency, singlet exciton formation branching ratio, triplet exciton formation branching ratio, PF efficiency, electron and hole recombination ratio respectively. According to Eq. (1), it can be seen that a smaller ΔE_{ST} will increase k_{RISC} . Besides, k_{RISC} is temperature dependent and a high temperature can promote the reverse intersystem conversion process.

$$k_{RISC} \propto e^{-\frac{\Delta E_{ST}}{k_B T}} \quad (2)$$

According to the quantum chemical theory, the singlet-triplet energy gap(ΔE_{ST}) can be expressed by $2J$, where

$$J = \iint \Phi_{HOMO}(r_1) \Phi_{LUMO}(r_2) \frac{1}{|r_2 - r_1|} \Phi_{HOMO}(r_2) \Phi_{HOMO}(r_1) \Phi_{LUMO}(r_1) dr_1 dr_2 \quad (3)$$

is an exchange integral which depends on the overlap of HOMO and LUMO, and the smaller overlap result in the smaller J value. A smaller J value leads to a smaller energy gap then a larger k_{RISC} . It seems that the smaller ΔE_{ST} is better, but according to the Franck-Condon principle, smaller overlap of HOMO and LUMO energy level will reduce the fluorescent radiative decay rate [6]. Thus, it is difficult to obtain smaller ΔE_{ST} and higher fluorescent radiative decay rate at same time. Therefore, one needs to design a proper molecular structure to meet the two properties meanwhile.

3. Progress

The design of TADF materials needs to meet these conditions as follows [17]: (1) Appropriate HOMO and LUMO energy level. Though a smaller overlap will lead to smaller singlet-triplet energy gap(ΔE_{ST}), it also results in a lower radiative decay rate. (2) A smaller singlet-triplet energy gap(ΔE_{ST}) so that triplet excitons are easy to up-convert into singlet excitons. (3) A high luminescence of singlet energy level and a stable triplet energy level, which can ensure the luminescence efficiency and reduce triplet exciton transmitting energy back to the ground state. (4) A bigger steric hindrance is necessary to better separate the energy levels of the two. (5) Stable structure and morphology of the molecule and a good film formation. (6) Good resistance to heat, light and electricity. The following will introduce the blue, green and red light materials, respectively.

3.1 Green TADF

The green radiation is centered on a wavelength of 532 nm with a color coordinate (CIE) of (0.26, 0.65) [16]. In 2015, Lee and his team provided a design approach of green material, TmCzTrz [18], which achieved a high EQE of 25%. Its CIE coordinate is (0.25,0.50). Subsequently, Kitamoto et al. proposed a luminescent compound consisting of 10H-phenoxaboryl group as an electron-accepting unit and phenoxazine as an electron-donating unit [19]. its experimental values of ΔE_{ST} was determined to be 0.028eV, which realized maximum η_{ext} of 22.1%. At present, TADF materials are usually fabricated by vacuum thermal evaporation which has a relatively expensive cost. In 2020, Hatakeyama et al. designed a MR-TADF emitter [20], OAB-ABP-1 via a four-step process involving one-shot double borylation, by solution process, which reduces the cost of fabrication. This material emits green light at 506nm with CIE coordinates of (0.12, 0.63), whose external quantum efficiency is relatively high, which is up to 21.8%. In 2021, Sasabe et al. designed two types of highly efficient ultra-pure-green TADF materials: DMac-BN and PXZ-BN. They used a one-pot borylation method by making simple modifications to a boron-nitro-gen skeleton without dangerous tert-Buli [21]. Table. 1 lists the summary of green TADF materials.

Table.1. Summary of green TADF materials

Compounds	λ (nm)	FWHM(nm)	PLQY	ΔE_{ST} (eV)	k_{RISC} (10 ⁴ s ⁻¹)	EQE _{max} (%)	CIE
TmCzTrz	500	—	100	0.07	—	25.5	(0.25,0.50)
DCzmCzTrz	496	—	98	0.2	—	21.3	(0.23,0.46)
phenoxazine	503	—	99	0.028	—	22.1	—
OAB-ABP-1	506	34	90	0.12	4	21.8	(0.12, 0.63)
DMac-BN	503	49	88	0.16	2.4	20.3	(0.18,0.60)
PXZ-BN	516	47	90	0.17	0.9	23.3	(0.22, 0.67)

3.2 Blue TADF

The blue radiation is centered on a wavelength of 450 nm, corresponding to an energy of 2.76 eV, with a color coordinate (CIE) of (0.17, 0.08) [16]. Conventional strategy of designing TADF molecule is introducing a donor and an acceptor [22, 23]. Hatakeyama et al. designed ultra-pure-blue TADF organic molecules (DABNA-1 and DABNA-2) [23], using triphenyl boron with two nitrogen atoms. Ahn et al. fabricated two highly efficient blue TADF materials, TDBA-Ac and TDBA-DI [24]. The TDBA-Ac device with PPBI host exhibited a deep-blue color with CIE coordinates of (0.15, 0.06), FWHM of 48 nm and a maximum EQE of 21.50%. The TDBA-DI devices have the performance of blue TADF emission with CIE of (0.15, 0.28) and a very high EQE of 38.15%. Besides, a higher RISC rate contribute to device stability and solving efficiency roll-off. In addition, small ΔE_{ST} and large spin-orbital coupling are required for efficient k_{RISC} . Gillet et al. reported a sky-blue metal-free organic emitter 5Cz-TRZ with a RISC rate of $1.5 \times 10^7 s^{-1}$, two orders of magnitude higher than the conventional emitters [25]. These materials exhibit a high EQE efficiency of 29.3% and a low efficiency roll-off at high luminance. Table. 2 lists the summary of green TADF materials.

Table.2. Summary of blue TADF materials

Compounds	λ (nm)	FWHM(nm)	PLQY	ΔE_{ST} (eV)	k_{RISC} (104 s-1)	EQE _{max} (%)	CIE
DABNA-1	459	28	0.88	0.2	0.99	13.5	(0.13, 0.09)
DABNA-2	467	28	0.897	0.2	1.48	20.2	(0.12, 0.13)
TDBA-Ac	458	48	0.93	0.06	99	21.5	(0.15, 0.06)
TDBA-DI	456	65	0.99	0.11	108	38.15	(0.15, 0.28)
5Cz-TRZ	—	—	—	0.02	1500	29.3	—

Table.3. Summary of red TADF materials

Compounds	λ (nm)	FWHM(nm)	PLQY	ΔE_{ST} (eV)	k_{RISC} (104 s-1)	EQE _{max} (%)	CIE
PXZ-DCPP	608	—	—	0.09	—	17.4	(0.56, 0.43)
PTZ-DCPP	640	—	—	0.18	—	12.3	(0.62, 0.36)
DCPPr- α -NDPA	606	—	90	0.07	—	31.5	(0.58, 0.42)
DCPPr- β -NDPA	616	—	77	0.08	—	27.1	(0.59, 0.40)
DCPPr-TPA	616	—	76	0.08	—	27.5	(0.59, 0.41)
DCPPr-DBPPA	622	—	73	0.08	—	25.4	(0.59, 0.40)

3.3 Red TADF

The red radiation is centered on a wavelength of 650 nm, corresponding to an energy of 1.91 eV, with a color coordinate (CIE) of (0.67, 0.33) [16]. Red luminescent materials are not developed as further as green and blue materials; thus, its non-radiative decay rate is particularly larger than green and blue materials [26]. In 2018, Wang et al. developed two novel hybrids via introducing DCPP [27], where the red emitters have small ΔE_{ST} values below 0.20 eV and radiate red lights with EL peaks at 608 and 640 nm with CIE coordinates of (0.56, 0.43) and (0.62, 0.36), respectively. In 2021, a series of DCPPr derivatives is proposed by Zhao et al. [26], where the device of DCPPr- α -NDPA nondoped emit NIR lights with peaks reaching 748 nm and high η_{ext} up to 1.9%, while the device of DCPPr- α -NDPA doped radiate red to deep red lights (606-652 nm) with a highest η_{ext} of 31.5%. Moreover, the host materials also employed an important role. In 2018, Kim reported 3PCzPFP [28] as a delayed fluorescence facilitating host for red-emitting HAP-3TPA which enhanced the EQE of

the red device up to 24.3%. At 1%, 3% and 5% doping concentrations, 3PCzPFP EL peak wavelengths devices were 577, 592, and 598 nm, respectively. Table. 3 lists the summary of green TADF materials.

4. Limitation and outlook

4.1 Limitation

At present, in order to inhibit the concentration quenching of its aggregate state and annihilation of exciton, TADF materials are usually only applied as a dopant in fluorescent devices [29], which is hard to ensure that there is no red or blue shift. Therefore, it is difficult to obtain ultra-pure luminescent color materials. Besides, although TADF materials is metal-free, without rare metal, it is not easy to achieve large-scale production due to its vacuum thermal evaporation technique. In addition, a high roll-off at high current density is also a problem. In addition, though the current luminous efficiency of blue and green light is higher, non-radiative decay increases as the light wavelength increases, while red light materials always have lower luminous efficiency than the other color lights. Thus, the way to fabricate efficient red-light materials is also important.

4.2 Future outlook

The research of TADF materials has made great progress and has been successfully applied to high-performance OLED. Among the TADF devices reported, it not only achieves a high external quantum efficiency, but also has the advantages of high color purity, long service life, low starting voltage. Besides, because it avoids to use precious metals, its cost is greatly reduced. Obviously, TADF will become the development trend of OLEDs in the future, but the intricate mechanism, more economical fabrication technique and higher efficient devices still need to be explored.

5. Conclusions

In summary, this paper discusses thermally activated delayed fluorescence materials from the perspective of progress in recent years. This paper introduced the development history and working mechanism of TADF materials and discussed the achievements of state-of-art approaches in these years divided into green, blue and red color respectively. The maximum external quantum efficiency of doped red color reached 31.5%, which is dramatically high efficiency. However, there are also some limitations. Nondoped materials is rare and the cost of fabrication is not economical. Donor units and acceptor units also need to be optimized and a better approach to separate LUMO and HOMO energy level needs to be explored as well. Nevertheless, there is no doubt that OLEDs is a very promising technology for display and TADF is one of the most important research fields in it. In the future, more and more donor and acceptor units will be investigated and the structure of TADF molecules will be ameliorated further. Overall, these results offer a guideline for subsequent studies in TADF.

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