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Review

Evolution of emission manners of organic light-emitting diodes: From emission of singlet exciton to emission of doublet exciton

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ABSTRACT

The emission manners of organic light-emitting diodes (OLEDs) have experienced almost three-decade evolution. In this review, we briefly summarized the emission manners of OLEDs including: (i) emission from singlet exciton; (ii) emission from triplet exciton; (iii) emission from singlet exciton converted from triplet exciton. Then we introduced a new type of OLEDs with the emission from doublet exciton, wherein organic neutral radicals are used as emitters. Due to the spin-allowed transition of doublet excitons, using neutral radicals as emitters is believed to be a new way to break the 25% upper limit of internal quantum efficiency of OLEDs. The progress of emissive stable neutral radicals is also shortly reviewed.

1. Introduction

Since Tang's innovative work in 1987 [1], organic light emitting diodes (OLEDs) have experienced nearly three-decades development and become one of the most promising technologies for flat-panel display and solid-state lightening sources due to the advantages of light weight, flexibility, and energy saving [2]. During the three-decade evolution of OLEDs, there are so many materials and devices that were reported. Although the diversity of materials and devices can be nearly infinite, their emission manners can be by far summarized as only three: (i) emission from the radiative transition of singlet excitons, corresponding to the fluorescent OLEDs [1]; (ii) emission from the radiative transition of triplet excitons, corresponding to the phosphorescent OLEDs [3]; (iii) emission from the radiative transition of singlet excitons converted from triplet excitons, corresponding to the OLEDs based on the mechanisms of thermally activated delayed fluorescence (TADF) [4], triplet–triplet annihilation (TTA) [5], hybridized local and charge-transfer (HLCT) emission [6] and triplet–polaron-interaction (TPI) induced upconversion [7]. It should be noted that all the light-emitting materials used in the OLEDs mentioned above are closed-shell molecules although their emission manners are different. Recently, a new kind of OLEDs using open-shell molecules such as neutral π-radicals as emitters wherein the emission comes from the radiative decay of doublet excitons was reported [8]. Because the transition back to the groud state of doublet excitons is spin-allowed, the transition problem of triplet excitons of fluorescent materials is thus circumvented.

2. Summarization of all kinds of OLEDs classified by the emission manners

It is known that 25% singlet excitons and 75% triplet excitons will be created when the injected hole and electron meet each other in the light-emitting region according to the simple spin statistics [9]. As shown in Fig. 1a, in OLED using traditional fluorescent materials as emitters, only singlet excitons can radiatively decay, and the triplets which account for 75% of the total excitons are wasted [9]. Thus the upper limit of internal quantum efficiency (IQE) which is defined as the ratio of the number of emitted photons to the number of injected charge carriers is 25%, given that the PL quantum yield of fluorescent materials is 100%.

To improve the IQE of OLEDs, efficient harvesting and utilizing the triplet excitons is always the most important issue in the following research of OLEDs. In 1998, the EL emission from triplet excited states of metal-to-ligand complexes made it possible to efficiently utilize triplet excitons *via* heavy metal effect [3a,3b]. In OLEDs based on metal-to-ligand complexes (phosphorescent materials), 100% IQE can be achieved due to that the spin-orbit

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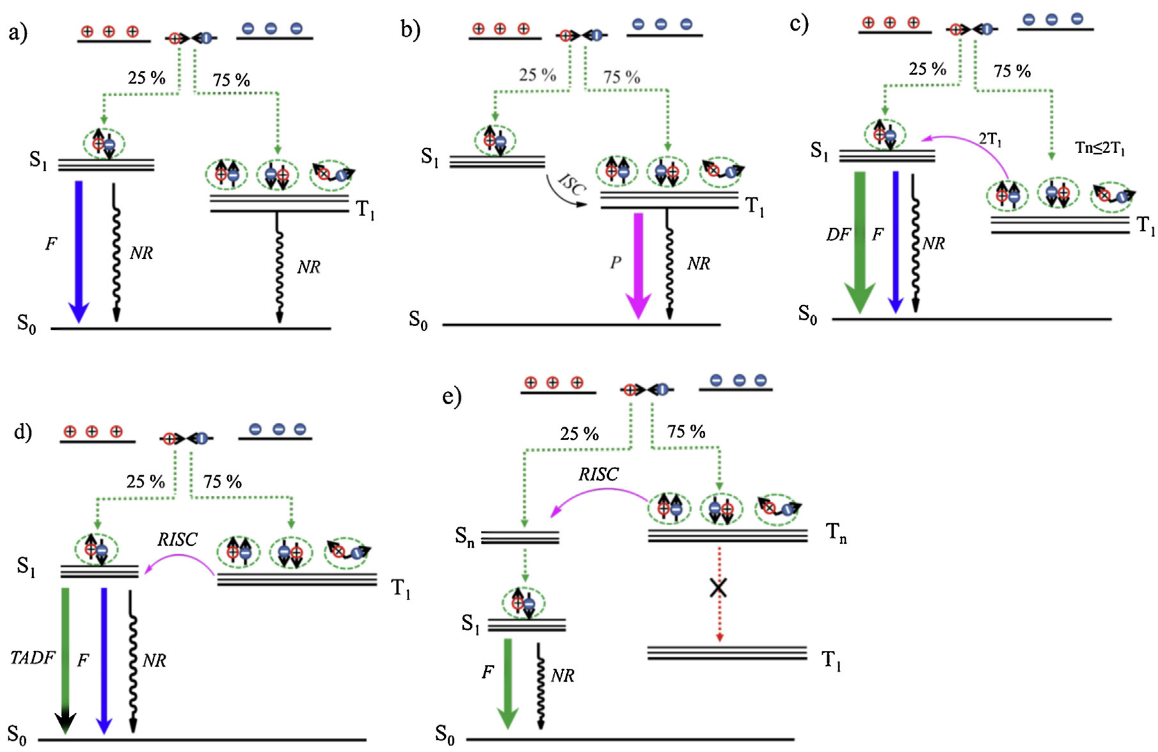

Fig. 1. Summary of triplet and singlet transition process in OLEDs. Fluorescence process (a); phosphorescence (b); triplet–triplet annihilation (TTA) (c); thermally activated delayed fluorescence (TADF) (d); hybridized local and charge-transfer (HLCT) emission (e); F, P, DF, NR, ISC, RISC represent fluorescence (F), phosphorescence (P), delayed fluorescence (DF), non-radiation process (NR), intersystem conversion (ISC), reverse intersystem conversion (RISC).

coupling effect of heavy metals enhances the transition possibility from T_1 to S_0 (Fig. 1b). Thus phosphorescent OLEDs containing heavy metals can overcome the problem of IQE upper limit of the conventional fluorescent OLEDs. However, phosphorescent OLEDs have some disadvantages, *e.g.*, room-temperature deep blue phosphorescent molecules are scarce, and the sky blue phosphorescent molecules always show instability during the vacuum evaporation and device operation [10]. Moreover, most of the useful heavy metals for phosphorescent materials are confined to iridium (Ir) and platinum (Pt), which are expensive and limited nature resources. As a result, production cost of the phosphorescent OLEDs is rather high.

In 1999, Cao *et al.* reported that the spin statistical limit of singlet formation ratio of 25% can be broken in the electroluminescence of some conjugated polymers [2a]. Shuai *et al.* proposed that the reverse intersystem crossing (RISC) can happen from triplet interchain polaron pair to singlet interchain polaron pair which are the precursors of triplet and singlet exciton, respectively, due to the strong interchain coupling [2b]. Other approaches to harvesting triplet excitons are TTA, TADF, HLCT and TPI induced upconversion that convert non-emissive triplet excitons to emissive singlet excitons. As shown in Fig. 1c, TTA is that two triplet excitons collide each other to form a ground state (S_0) and a singlet exciton (S1) ($2T_1 > S_1$), which causes the P-type delayed fluorescence. Ideally, the upper limit of IQE of the devices *via* TTA process can be enhanced to 62.5% [11].

The first application of TADF in OLEDs was reported by Adachi *et al.* in 2009 [4a]. In TADF process, as shown in Fig. 1d, extremely small energy gap between S_1 and T_1 (ΔE_{ST}) is required to benefit RISC from T_1 to S_1 through thermal activation. In this way 75% non-emissive triplet excitons can be efficiently utilized, resulting in 100% IQE of TADF-based OLEDs. To design TADF molecules, spatial separated distribution between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is needed, which is matched by the donor–acceptor (D–A) type structure [4c,12]. However, D–A architecture often leads to intramolecular charge transfer (ICT) property that is not beneficial to achieve blue TADF materials and high PL quantum yield. Another problem is that TADF-based OLEDs have serious efficiency roll off as operation voltage increases [13].

Another feasible method to harvest triplet excitons is HLCT emission (Fig. 1e). By using moderate donor (D) and accepter (A) groups and controlling the steric hindrance between D and A, a new state can be obtained in which charge transfer (CT) state and locally excited (LE) state simultaneously exist in a molecule. LE part has the large transition moment and CT part can enhance the S_1 component through RISC between high-lying triplet and singlet excited states [6a,6b,14].

Recently, we reported a new possible way to harvest triplet excitons through TPI-induced upconversion [7]. Different from that TADF and HLCT benefit from the RISC processes at the lowest- and higher-level excited states, respectively, and the spin angular momentum is not conserved, TPI induced upconversion is a intermolecular process. It has two distinct characteristics: (i) TPI is a spin conserving process, *i.e.* the spin-flip does not need; (ii) TPI can occur circularly, that is TPI can continuously convert triplet to singlet, which may induce much higher singlet ratio in OLEDs.

It should be noted that all the emitters used in the OLEDs based on the mechanisms of phosphorescence, TTA, TADF, HLCT and TPI-induced upconversion are all closed-shell molecules. Last year, we demonstrated the possibility using neutral open-shell molecules as the emitter of OLEDs in which the emission comes from the doublet excitons [8].

3. Neutral π-radical-based OLEDs

For conventional luminescent materials (closed-shell molecules), their HOMO is filled with two electrons with opposite spin

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