A New Route of Triplet Harvesting for High-Efficiency Organic Light-Emitting Diodes

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Triplet exciton harvesting is a key issue for high-efficiency organic light-emitting diodes (OLEDs). Recently, we demonstrated an alternative pathway for efficient fluorescence-based OLEDs by applying thermally activated delayed fluorescence (TADF) as a singlet energy generation mechanism using materials with a small energy gap between singlet and triplet excited states. The resulting fluorescence-based OLEDs with TADF materials as dopants showed very high internal electroluminescence quantum efficiencies approaching nearly 100% for blue, green, yellow, and red emission. We also found that the OLEDs employing this triplet energy harvesting process have significantly enhanced device operational stability. In this article, we will review the unique features of this triplet harvesting process, i.e., TADF-assisted fluorescence.

Keywords: Organic light-emitting diodes, Thermally activated delayed fluorescence (TADF), Energy transfer process, TADF-assisted fluorescence

1. Introduction

Since organic light-emitting diodes (OLEDs) are anticipated to play a major role in next-generation displays and general lighting sources because of their unique advantages of high electroluminescence (EL) efficiency, wide viewing angle, high contrast, high-speed response, large area and light weight, OLEDs have been extensively studied over the past twenty-five years. Research of OLEDs has focused on the development of both various organic light-emitting materials and device architectures for efficient devices.

The EL in OLEDs arises from the radiative decay of excitons that are formed by the charge carrier recombination of injected hole and electron carriers. The external EL quantum efficiency (η) of OLEDs is once of the most important performance parameters and is described by the well-known equation:

\[ \eta_{\text{ext}} = \eta_{\text{in}} \times \eta_{\text{eff}} \times \eta_{\text{mix}} \times \eta_{\text{out-coupling}} \]  

(Eq. 1)

where \( \eta_{\text{in}} \) is the internal EL quantum efficiency and \( \eta_{\text{out-coupling}} \) is the light out-coupling efficiency. According to Eq. (1), \( \eta_{\text{in}} \) is limited by the following three factors: i) the charge balance of injected holes and electrons (\( \eta_{\text{in}} \)), ii) the efficiency of radiative exciton production (\( \eta_{\text{eff}} \)), and iii) the photoemission (PE) quantum yield of the emitter molecules (\( \eta_{\text{mix}} \)). An ideal \( \eta_{\text{in}} \) of unity can be achieved by careful design of OLED structures with the appropriate selection of charge transport layers, host–guest system, and anode and cathode materials. In addition, by designing molecules for optimal light emission, \( \Phi_{\text{em}} \) of nearly 100% has been demonstrated in a wide variety of organic light-emitting materials.

Since spin statistics states that one singlet exciton is generated for every three triplet excitons upon the recombination of holes and electrons in an organic material, \( \eta_{\text{in}} \) strongly influences \( \eta_{\text{ext}} \). These excitons have two possible radiative decay pathways to produce EL: from a singlet (S) or triplet (T) excited state to the ground state as "fluorescence" or "phosphorescence", respectively. However, the spin-antisymmetry of the ground state tends to prevent the efficient radiative decay of triplet excitons, resulting in \( \eta_{\text{in}} \) severely limiting \( \eta_{\text{ext}} \) if the 75% of electrically generated excitons formed in triplet states are not harvested. Therefore, only a few materials, such as iridium complexes, exhibit efficient EL, which results from the presence of a heavy atom promoting the mixing of the spin orbitals of singlet and triplet states.

Thus, the key issue for achieving high efficiency is the harvesting of triplet excitons for light emission, and the use of molecules exhibiting high efficiency phosphorescence at room temperature resulted in emission from nearly 100% of the generated excitons. Although these unique light-emitting molecules are a promising technology in OLEDs, fluorescence-based OLEDs continue to attract interest because of their long operational lifetimes, high EL color purity, and potential to be manufactured at low-cost in next generation full-color display and lighting applications. Therefore, a method to achieve high efficiency using a wide variety of existing common "fluorescent" molecules as the emitting component would be of
great value. Phosphorescence-sensitized fluorescence, which has been realized by energy transfer from the T1 state of a phosphorescent emitter such as an iridium 2-phenylpyridine complex to the S1 state of a fluorescent emitter via dipole–dipole coupling (i.e., Förster energy transfer, FRET), is one possible way to obtain highly efficient OLEDs based on a fluorescent emitter. However, the FRET process from T1 of an exciton donor to S1 of an exciton acceptor is generally a spin forbidden transition, indicating that the FRET is inefficient. Another route is generation of singlet excitons via a triplet–triplet annihilation (TTA) process. For example, some OLEDs containing anthracene and tetracene derivatives showed rather high quantum efficiency because the classical theoretical limit of singlet excitation formation of 25% was exceeded, resulting in quantum yield of TADF of 7%–11%. However, the theoretical upper limit for the yield of singlet excitons generated from triplets in a TTA process is <0.5, which confines the maximum quantum yield to <62.5%.

Recently, our research group has proposed an alternative route to achieving quantum yield of 100% using a new light-emitting mechanism called thermally activated delayed fluorescence (TADF). Triplet harvesting using TADF, recognized as the “third-generation” of organic light-emitting diodes (OLEDs), is a rapidly growing field and one of the most promising routes for achieving highly efficient fluorescent OLEDs. Furthermore, we recently designed a novel device architecture with the proper combination of TADF molecule as a singlet exciton generator and fluorescent molecule as an end emitter. i.e., TADF-assisted fluorescence, hereafter abbreviated as TAF. That enables quantum efficiency of nearly 100% from conventional fluorescent emitters and has great potential for improving operational stability. In the TAF system, after carrier recombination and formation of both singlet and triplet excitons on TADF assistant dopants, the triplet excitons are up-converted to the singlet state. Singlet excitons in the TADF molecules are then transferred to fluorescent guest molecules via a Förster process and emit light by radiative decay from a singlet state of the fluorescent guest molecule. Based on this concept, we demonstrated highly efficient fluorescence-based OLEDs with 100% of excitons yielding light emission. In this article, we will review the unique features of TAF-OLEDs.

2. The features of TAF

2.1 Basic concept of TADF

The up-conversion process of triplet excitons to singlet excitons using thermal energy has long been known as E-type delayed fluorescence in the field of photochemistry. To obtain efficient TADF, a small energy gap between S1 and T1 states (ΔESt) is essentially required, which is realized in molecules possessing little overlap of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Recent design of molecules that exhibit TADF has been based on the combination of donor and acceptor units, which has achieved ΔESt comparable to or less than the thermal energy of 27 meV at 300 K. In this way, our research group produced high-efficiency OLEDs by using the TADF process and achieved an quantum efficiency of 20%, comparable to those of phosphorescent OLEDs. More details of the molecular design and light-emitting mechanism of TADF materials were well reviewed by one of us.

2.2 Basic concept of TAF

Triplet harvesting using TADF, recognized as the “third-generation” of OLEDs, is a rapidly growing field and one of the most promising routes for achieving highly efficient fluorescent OLEDs, with applications from flexible displays to high-efficiency lighting. However, TADF-OLEDs unfortunately still face issues related to a large triplet population during electrical excitation such as a rather strong decrease of efficiency at high luminance, which is caused by exciton annihilation arising from triplet-singlet interactions, and poor operational stability. To solve these problems, we define guidelines for and demonstrate the dual enhancement of quantum efficiency and operational stability in OLEDs incorporating TADF molecules as “assistant” dopants, i.e., TADF-assisted fluorescence.

Fig. 1 shows our proposed energy transfer mechanism for the TAF system. In the case of a conventional host-guest system, i.e., the combination of fluorescent host and fluorescent emitter, the singlet excitons formed on the fluorescent host molecules are immediately transferred to the S1 state of fluorescent emitter molecules via FRET, but the triplet excitons on the fluorescent host molecules are completely deactivated to the ground state due to the large ΔESt of the
materials. In addition, injected carriers are also likely to be trapped on emitter dopants due to their shallower HOMO and deeper LUMO compared to those of the host material, leading to direct carrier recombination on the emitter dopants. Therefore, no triplet excitons contribute to the total EL efficiency. According to Eq. 1, the theoretical limit of $\eta_{\text{el}}$ for a conventional fluorescent emitter in a host–guest matrix is only 5%, assuming that $\gamma = 1$, $\eta_A = 0.25$, $\Phi_L = 10$, and $\eta_{\text{exc}} = 0.2$.

Conversely, in the case of a TAF system using TADF materials as singlet energy converters, i.e., a double-dopant system (host material, a TADF dopant, and a fluorescent emitter dopant), the electrically generated triplet excitons on TADF molecules are up-converted through a reverse intersystem crossing (RISC) process allowed by the small $\Delta E_{\text{ST}}$ of the TADF materials (generally, $\Delta E_{\text{ST}} < 0.1 \text{ eV}$). Therefore, triplet excitons can be harvested by conversion to singlet excitons and subsequent energy transfer from the $S_1$ state of the TADF materials to the $S_1$ state of fluorescent emitters via FRET. Thus, the theoretical limit of $\eta_{\text{el}}$ can be overcome while still using common fluorescent emitters, leading to a maximum $\eta_{\text{el}}$ of 100% in principle.

2.3 Design of emissive material layer for TAF-OLEDs

In the TAF system, since direct carrier recombination on fluorescent emitters limits the utilization of triplet excitons due to the rather large $\Delta E_{\text{ST}}$ of conventional fluorescent molecules, the doping concentration of the fluorescent emitter dopants should less than 1 wt%. On the other hand, TADF assistant dopants should be doped into the emissive material layers.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** Photoluminescence characteristics of TADF and emitter dopants and chemical structures of the assistant dopants used in this study. Fluorescence spectra of assistant dopant: host co-deposited film (upper), and absorption (dashed line) and fluorescence (solid line) spectra of emitter dopant in solution. 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.
(EMLs) in rather high concentrations, i.e., 15-99 wt%, which ensures that the TADF assistant dopants act as the main carrier recombination centers in the EMLs, allowing the created triplet excitons to up-convert to singlet energy on the TADF molecules. In addition, to achieve efficient transfer of the singlet energy generated from a triplet on a TADF molecule to a fluorescent exciton acceptor, large spectral overlap between the ground state absorption of the exciton acceptor, i.e., fluorescent molecules, and the fluorescence emission of the exciton donor, i.e., TADF assistant dopants, is required.

Here, we also mention that the effect of direct triplet energy transfer. In the TADF system, the energy transfer from S1 of a TADF molecule to S1 of a fluorescent molecule, i.e., Förster energy transfer, is very efficient, but the direct triplet energy transfer from T1 of a TADF molecule to T1 of a fluorescent molecule, i.e., Dexter energy transfer, should be considered as an additional energy loss process. However, since the Dexter energy transfer process is well known to be a short-range interaction process, dispersing the TADF assistant dopants in a host matrix, i.e., using a double-doping system, can prevent Dexter energy transfer due to an increase of the average distance between an exciton donor molecule and an exciton acceptor molecule. In fact, although a rather high η of nearly 10% was achieved in a fluorescent OLED with a TADF material as the host matrix, the η gradually increased with a decrease of the concentration of TADF molecules by introducing a separate host material, resulting in a maximum η approaching 20%, indicating the suppression of Dexter energy transfer.

3. Photoluminescence characteristics of TADF thin films

Fig. 2 shows the emission spectra of the TADF assistant dopants and the absorption spectra of the conventional fluorescent emitters for some example TADF systems. Since these combinations show large spectral overlap between the absorption of the exciton acceptor and the PL of the exciton donor, efficient FRET of singlet excitons is possible. For example, a large Förster transfer radius ($R_0$) of ~6.9 nm for the 1 wt% -2,8-di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb) : 15 wt% -2-phenoxazine-4,6-diphenyl-1,3,5-triazine (PXZ-TRZ) : 3,3-di(9H-carbazol-9-yl) biphenyl (mCBP) system was estimated, suggesting that efficient FRET is possible; indeed, only yellow emission from TBRb was observed from these co-deposited films. The co-deposited films exhibited $\Phi_\text{ET}$ of 80±3%, indicating that the efficiency of energy transfer ($\Phi_\text{ET}$) from the S1 state of the exciton donor (PXZ-TRZ) to the S1 state of the exciton acceptor (TBRb) is very efficient under optical excitation.

To confirm that the conversion and transfer of triplet energy from the TADF assistant dopant to the fluorescence emitter occurs, the transient PL characteristics were measured, and considerable differences between the transient PL for the host-guest matrices with and without TADF assistant dopants were observed. For example, while only a prompt component with a transient decay time ($\tau_p$) of ~18 ns was seen for the 1 wt% -TBRb : mCBP film, a delayed component with a transient decay time ($\tau_d$) of ~1 μs was clearly observed in addition to $\tau_p$ of ~16 ns for the 1 wt% -TBRb : 15 wt% -PXZ-TRZ : mCBP co-deposited film (Fig. 3). The emission spectrum of the delayed component was identical to that of the prompt one, which originates from TBRb and provides evidence of the contribution of T1 states from the PXZ-TRZ molecules.
In the 1 wt%-TBRb : 15 wt%-PXZ-TRZ : mCBP film, since the rate constant of energy transfer from exciton donor to exciton acceptor, $k_{\text{ET}} = \frac{1}{\tau_d R^6}$, where $\tau_d$ is the radiative decay time of the donor molecule and $R$ is the average distance between donor and acceptor molecules, is nearly two orders of magnitude faster than those of the intersystem crossing (ISC) and RISC processes, the singlet excitons of PXZ-TRZ generated by photo-absorption are mainly promptly transferred to the S1 state of TBRb via FRET. However, some of the PXZ-TRZ singlet excitons decay to the T1 state through ISC and are up-converted back to the S1 state by thermal conversion, followed by energy transfer via FRET to the S1 state of TBRb that then produces the delayed emission.

4. Characteristics of TAF-OLEDs

To demonstrate the benefits of energy transfer by exciton up-conversion from T1 to S1 states under electrical excitation by using a TAF-system, we fabricated fluorescent-emitter-based OLEDs with TADF molecules as assistant dopants. We also fabricated reference OLEDs containing only fluorescent emitters. The $\eta_{\text{max}}$-luminance ($L$) characteristics of the OLEDs are shown in Fig. 4. The OLEDs without TADF assistant dopants which use only conventional single doping by fluorescent dopants, exhibit low device performance ($\eta_{\text{max}} < 5$%), indicating that the electrically generated triplet excitons on the fluorescent emitters do not contribute to the total EL intensity. On the other hand, very high $\eta_{\text{max}}$ of $>13$% over the full visible range were achieved in the TAF-OLEDs.

Next, we examine $\eta_{\text{max}}$ in these TAF-OLEDs. Since high $\Phi_{\text{T}}$ of $80 \pm 2$%, $81 \pm 2$%, $90 \pm 2$%, and $88 \pm 2$% were obtained for the fluorescent emitter dopants of 25,811-tetra-tert-butylperylen-9,10-bis-[N,N-di-(p-tolyl)-amino]anthracene (TTPA), TRBs, and tetraphenylethenediindenoperiflanthene (DBP), respectively, when doped with TADF assistant dopants in a host matrix, we can estimate $\eta$ of $55-84$%, $65-97$%, $66-100$% and $66-99$%, respectively, assuming a charge carrier balance factor of unity and a light-out-coupling efficiency of 20-30%. These results clearly indicate that the devices overcame the theoretical limit of 25% for the singlet exciton production efficiency that is assumed for fluorescent-emitter-based OLEDs. Fig. 5 shows the EL spectra of the OLEDs. These OLEDs emit a full range of visible colors from blue to red originating from the fluorescence emitter dopants. In addition, the emission from the TADF assistant dopants almost disappeared, and a current-independent EL spectrum was observed for all of the OLEDs. These results indicate that very efficient energy transfer of singlet excitons from exciton donor to exciton acceptor occurs under electrical excitation.

An enhancement of color purity for EL is also possible by using TAF. In general, since the nature of TADF emission is a charge-transfer (CT) state that forms between an electron-donating and electron-accepting unit of a TADF molecule,
almost all TADF materials show broad emission spectra with rather large full widths at half-maximum (FWHM) of about 100 nm, which is quite a bit wider than those of conventional fluorescent materials. Fig. 6 shows the emission and absorption spectra of a blue fluorescent emitter, TBPe, and a compatible TADF assistant dopant, 10-phenyl-10H,10'H-spiro[acridine-99'-anthracene]-10'-one (ACRSA). Although the 15 wt% ACRSA : DPEPO co-deposited film showed sky-blue emission with a peak emission wavelength of ~490 nm, the onset of emission (~430 nm) is at a wavelength that is markedly shorter than the emission peak, indicating an S1 state for ACRSA emission (430 nm) is at a wavelength that is markedly shorter than the emission peak, indicating an S1 state for ACRSA (~2.89 eV) is slightly higher than that of TBPe (~2.69 eV). Thus, the 1 wt% TBPe : 15 wt% ACRSA : bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) co-deposited film showed pure blue emission with a peak emission wavelength of ~460 nm, and the Commission Internationale de l’Eclairage (CIE) coordinates of the OLED changed from (0.23, 0.42) to (0.16, 0.29) by doping with TBPe molecules while maintaining a high η of over 13%.

Time-resolved EL measurements of the OLEDs provides conclusive evidence for energy transfer in conversion from T1 to S1 states in the TADF molecules. For example, Fig. 7 illustrates the transient decay curves obtained for yellow OLEDs with an EML of 1 wt% TBBrb in a PXZ-TRZ host or a conventional fluorescent host matrix, tris(8-hydroxyquinolinato)aluminum (Alq3). For the OLED with the Alq3 host, the EL intensity decayed rapidly after the excitation pulse, suggesting that there was no contribution of the triplet excitons in the conventional host–guest system. In contrast, we clearly observed a delayed component with a τd of ~14 μs for the OLED with the PXZ-TRZ host, which was close to that obtained for the PXZ-TRZ-only OLED (τd ~16 μs), indicating that PXZ-TRZ triplet excitons contributed substantially to emission from this OLED. In addition, the emission spectrum of the delayed component was identical to that of the prompt component, indicating that the delayed EL originates from the S1 state of TBRb. Although the contribution of the delayed fluorescence to the total PL intensity was small (Φd ~11%), the delayed fluorescence was a large proportion of total EL intensity for the OLED under electrical excitation. This difference can be attributed to the direct formation of triplet excitons under electrical excitation. Similar transient EL behavior was also observed in the TAF-OLEDs based on a double-doped system.

5. Device operational stability

The ability to manufacture high EL efficiency OLEDs with long device operational lifetimes is one of the most important and challenging problems for both scientific and industrial development. Recently, we demonstrated green TADF-OLEDs exhibiting promising operational stability with an LT50 (continuous operation time until the initial luminance decays by 50%) of over 2,500 hours for an initial luminance of 1,000 cd/m², indicating that properly designed TADF molecules are intrinsically stable even under electrical excitation. However, the possibility for the rather long exciton lifetime of the triplet excited states to cause reduced operational stability due to an increased chance for unwanted chemical reactions has been a concern. Therefore, to achieve higher operational stability in TADF-based OLEDs, the reduction of the triplet exciton population is desired. In fact, we observed that the introduction of fluorescent molecules into a system with a conventional fluorescent host and a TADF guest provides not only a significant enhancement of η but also an enhancement of device operational stability under electrical excitation.

For example, Fig. 8 shows the normalized EL intensity of a TADF-OLED (15 wt%-PXZ-TRZ : mCBP as EML) and a TAF-OLED (1 wt%-TBBrb : 15 wt%-PXZ-TRZ : mCBP as EML) as a function of operating time at a constant current density of 10 mA/cm². We found that the operational lifetime (LT50) of the TADF-OLED was over 50% longer than that of the TAF-OLED while the voltage-rise curves are almost the same for both OLEDs as shown in the inset of Fig. 8. Similar behavior of the enhancement of device stability was also observed in all TAF-OLEDs, clearly indicating that the TAF system provides a general route to enhance an OLED stability.

6. Outlook

Our new concept of triplet harvesting, which is up-conversion of a triplet exciton to the singlet state in a TADF molecule, induced efficient radiative decay of singlet excitons on common fluorescent emitters under electrical excitation. As a result, η overcame its theoretical limitation of 25% using
common fluorescent emitters, leading to a maximum quantum efficiency of 100% in principle. Since numerous fluorescent molecules with both very high \( \Phi_F \) and high color purity already exist, our mechanism provides a flexible OLED architecture that can achieve highly efficient EL comparable to that of well-established OLEDs using phosphorescence-and TADF-based emitter materials. In addition, we note that our proposed triplet energy harvesting processes can be applied not only to conventional fluorescent emitters but also phosphorescent emitters. Therefore, this concept provides an important general method to realize full color displays and lighting sources with high efficiency and high operational stability.

References
35) H. Nakanotani, unpublished work

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