Reverse intersystem crossing from upper triplet levels to excited singlet: a ‘hot excition’ path for organic light-emitting diodes

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Since researches on the fate of highly excited triplet states demonstrated the existence of reverse intersystem crossing (RISC) from upper triplet levels to singlet manifold in naphthalene, quinoline, isoquinoline, etc. in the 1960s, this unique photophysical process was then found and identified in some other aromatic materials. However, the early investigations mainly focus on exploring the mechanism of this photophysical process; no incorporation of specific application was implemented. Until recently, our group innovatively used this ‘sleeping’ photophysical process to enhance the efficiency of fluorescent organic light-emitting diodes by simultaneously harvesting singlet and triplet excitons. Efforts are devoted to developing materials with high photoluminescence efficiency and effective RISC through appropriate molecular design in a series of donor–acceptor material systems. The experimental and theoretical results indicate that these materials exhibit hybridized local and charge-transfer excited state, which achieve a combination of the high radiation from local excited state and the high $T_m \rightarrow S_n$ ($m \geq 2$, $n \geq 1$) conversion along charge-transfer excited state. As expected, the devices exhibited favourable external quantum efficiency and low roll-off, and especially an exciton utilization efficiency exceeding the limit of 25%. Considering the significant progress made in organic...
light-emitting diodes with this photophysical process, we review the relevant mechanism and material systems, as well as our design principle in materials and device application.

1. Introduction

Reverse intersystem crossing (RISC) that is defined as a process of energy transfer from the excited triplet state back to the singlet is an important photophysical process [1]. Materials with efficient RISC could be used to increase the efficiency of fluorescent organic light-emitting diodes (FOLEDs) by harvesting singlet and triplet excitons simultaneously. Generally, this RISC occurs primarily from the lowest excited triplet state ($T_1$) to the lowest excited singlet state ($S_1$) of a molecule according to Kasha’s rule [2]. Well-known examples of such RISC include the compounds with E- and P-type delayed fluorescence properties. E-type molecules usually possess a much smaller energy gap between $S_1$ and $T_1$, which allows the conversion of $T_1$ excitons into the radiative $S_1$ excitons through the thermally activated RISC (also called thermally activated delayed fluorescence, TADF) [3]. As for the P-type delayed fluorescence, the activation energy is provided by triplet–triplet annihilation (TTA), and therefore it does not require the small energy gap between $S_1$ and $T_1$ [4].

In some cases, RISC can also occur from upper triplet levels where intersystem crossing (ISC) to the singlet manifold competes with direct internal conversion (IC) to $T_1$ [5]. Previous photophysical researches in some organic compounds have revealed and identified the existence of this photophysical process by the two-step two-colour laser technique [6]. This unique photophysical process should be also used in increasing the efficiencies of FOLEDs similar to the TADF and TTA materials. Here, we define the RISC process involving the low-lying excited states ($T_1 \rightarrow S_1$) as a ‘cold exciton’ process (for example, TADF and TTA mechanism), whereas the process involving high-lying excited states ($T_m \rightarrow S_n$, $m \geq 2$, $n \geq 1$) is defined as a ‘hot exciton’ process. And ‘hot exciton’ process for FOLEDs may show some advantages over ‘cold exciton’. For example, TADF and TTA inevitably suffer from the problem of triplet–triplet or singlet–triplet quenching due to the accumulated $T_1$ excitons (the low RISC rate), while the RISC from ‘hot exciton’ process can quickly transfer triplet in high levels to singlet states and avoid the accumulation of triplet exciton in $T_1$ states. Unfortunately, the reported materials with RISC from ‘hot exciton’ process usually show low photoluminescence (PL) efficiencies and are difficult to be used as emitters for FOLEDs. Recently, our group found that some donor (D) and acceptor (A) constructed materials also showed RISC from hot exciton path [7,8]. These materials demonstrated a hybridized local and charge-transfer (HLCT) state, resulting in high PL efficiencies and effective RISC from upper triplet levels to singlet. As expected, the breakthrough of exciton statistics limit (25%) is confirmed by the high exciton utilization efficiency of the FOLEDs based on these materials. Due to the important application of RISC from upper triplet levels in FOLEDs, in this review article, we summarized the basic mechanism of RISC from upper triplet levels, the material systems with this photophysical process, as well as our new design principles of materials that combine high PL efficiencies together with effective RISC from upper triplet levels to singlet.

2. Early investigation and mechanism of reverse intersystem crossing from upper triplet levels

Since the electronic transitions from excited triplet states to higher excited triplet states in aromatic molecules were first observed and identified by Lewis and Lipkin in 1942 [9], interest in the fate of these highly excited triplet states has been widely expressed by researchers [10]. One possible path for the decay of these highly excited triplet states was predicted to be RISC into the singlet manifold and IC to the lowest excited singlet state. Until 1969,
this presumable excited triplet–singlet ISC was experimentally confirmed by Keller based on the observation of weak fluorescence emission in several aromatic molecules, such as naphthalene, quinoline, isoquinoline, etc. after photo-excitation of metastable $T_1$ [5]. Here, this weak fluorescence emission is identical to their continuous-wave fluorescence spectra, an indication of radiation decay from $S_1$. However, because Keller’s method is excited with a steady-state excitation source, it is difficult to obtain detailed information about the mechanisms of this photophysical process.

Due to the development of two-step two-colour laser technique, more and more organic materials are found showing such fluorescence when they are excited by a first laser with short wavelength and then probed by a second excitation of low-energy laser at a certain delayed time after the first laser pulse [11]. It should be emphasized that the excitation wavelength of the first laser in the experiment is in resonance with the $S_0 \rightarrow S_1$ transition, whereas the excitation wavelength of the second laser (probe pulse) is only resonant with the $T_1 \rightarrow T_m$ transition. This pronounced emission was only detected in two-colour, two-pulse experiments, namely two-step laser-induced fluorescence (TSLIF), and it did not occur when the second low-energy laser pulse was alone incident on the sample. These TSLIFs are further evidenced to originate from the RISC from upper triplet levels to singlet levels instead of TADF and TTA mechanisms by the following experimental results [6]. First, the energy gap between $S_1$ and $T_1$ was estimated to be very large in most of these compounds; thus, it is difficult to achieve the thermally activated RISC. Second, the intensity of this delayed fluorescence depends linearly on the population of the triplet state, instead of the square characteristic of this population in TTA process. Third, no emission was observed if only the first excitation pulse is applied (detection between pulses), which is contrasted with TADF and TTA. Fourth, the intensity of this delayed fluorescence increases with the probe pulse energy. Therefore, the previously speculated RISC from upper triplet levels to excited singlet states, $T_m \rightarrow S_n \rightarrow S_1$ ISC ($m \geq 2$, $n \geq 1$), should be responsible for this kind of delayed fluorescence. A schematic description of this excited state process is shown in figure 1. After excitation by the first laser pulse, the ISC causes the conversion from the singlet states to the triplet states and the consecutive relaxation processes lead to a significant population of the lowest triplet state $T_1$ [2]. By irradiation with the probe pulse for a delayed time less than the lifetime of the triplet state $T_1$, a certain fraction of the triplet population is promoted to a higher triplet state, $T_m$. Due to the cooperation of large $T_1$–$T_2$ energy gap, energetic closeness between $T_m$ and $S_n$, heavy atom effect, etc., RISC from the higher triplet states into the singlet manifold can successfully compete with the IC leading back to $T_1$. Therefore, delayed fluorescence was consequently observed from the radiative decay of the lowest singlet state formed via RISC.

**Figure 1.** Energy level diagram for RISC from upper triplet levels to singlet levels. (Online version in colour.)
3. Previous material systems with reverse intersystem crossing from upper triplet states

In the past four decades, several types of organic materials with RISC from upper triplet levels have been reported, such as anthracene derivatives [12], organic dyes [13], excited-state intramolecular proton transfer (ESIPT) materials [14–16], etc. The chemical structures of some representative materials are shown in figure 2.

Anthracenes are representative examples of molecules showing TSLIFs [17]. Early researches on meso-substituted anthracenes found that their fluorescence yields increase with decreasing temperature and no triplet formation can be detected at 77 K [18,19]. These facts are explained by thermally activated ISC from $S_1$ to $T_2$. Out of interest in this ISC from $S_1$ to $T_2$, Kobayashi et al. [20] found that the RISC from $T_2$ to $S_1$ also occurred when the metastable $T_1$ was further excited into higher triplet states. Through systematical study, they established the quantum yields of $T_2 \rightarrow S_1$ ISC ($\Phi_{ts}$) of anthracene, 9-methylanthracene, 9-phenylanthracene, 9,10-dichloroanthracene and 9,10-dibromoanthracene to be $2.6 \times 10^{-5}$, $3.6 \times 10^{-4}$, $4.7 \times 10^{-4}$, $1.5 \times 10^{-2}$ and $2.7 \times 10^{-1}$, respectively. The significant increases of $\Phi_{ts}$ in meso-derivatives are interpreted in terms of level inversion of $T_2$ and $S_1$ due to the substitution at the meso-position, assuming that $S_n \leftarrow T_1$ absorption cross section is negligible in comparison with $T_m \leftarrow T_1$ absorption cross section. As for the halogenated anthracenes, the increased $\Phi_{ts}$ could be attributed to the internal heavy atom effect.

The RISC from upper triplet levels is also observed in some organic dyes [21], such as flavins [6], cyanine derivatives [13], erythrosin B, rose bengal and tetraphenylporphyrin [22,23]. Hub and co-workers reported that the flavin 10-phenylisoalloxazine can be excited with a sequence of two intense laser pulses ( interpulse separation) of 337 and 580 nm, respectively, and the delayed fluorescence emission around 540 nm was detected. From the saturation effect of probe pulse
induced emission intensity versus probe pulse energy, they derived an estimation of $\Phi_{ts}$ to be $8 \times 10^{-3}$. They further verified some other isoalloxazine derivatives also demonstrated TSLIFs, indicating of that RISC $T_m \rightarrow S_n$ is characteristic of isoalloxazines. The complicated photophysical processes of cyanine dyes also involved RISC from upper triplet levels. Redmond et al. observed TSLIFs in three cyanine dyes, merocyanine 540, BO-Se and QI-Se. The ratios of RISC to IC in promoted higher excited triplet state are estimated to approximately 0.7 for all cyanines, indicative of only 30% IC from $T_m$ back to $T_1$. The origin of RISC from upper triplet levels may be ascribed to both a large $T_2$-$T_1$ energy gap and the effect of heavy atom substitution (S, Se). Beside the flavins and cyanine dyes, Reindl and Penzkofer found that erythrosin B, rose bengal and tetraphenylporphyrin also show RISC from upper triplet levels [22,23].

ESIPT materials are another series of materials showing RISC from upper triplet levels. As shown in figure 3, the photophysical processes of ESIPT materials usually involve an intrinsic four-level cyclic proton-transfer reaction ($E \rightarrow E^* \rightarrow K^* \rightarrow K \rightarrow E$). Itoh and Chou groups have explored photophysical properties of a series of ESIPT materials, such as 2-(2′-hydroxyphenyl)-benzothiazole (HBT) [25], 3-hydroxyflavone [26,27], 7-hydroxy-1-indanone (7HIN) [24], etc., by the transient absorption and the two-step two-colour laser technique. Taking 7HIN as an example, a tentative mechanism of the complete photophysical process of TSLIF is schematically shown in figure 3. After excitation of the first pulse, the excited states of cis-enol form quickly evolve to excited states of cis-keto form accompanying proton transfer. It has been reported that in the tautomer form of 7HIN, the $S'_{\pi\pi^*}$ and $T'_{\pi\pi^*}$ states are possibly much higher in energy than the $T'_1$ ($\pi\pi^*$) states. As a result of the large spin–orbit coupling between $T'_{\pi\pi^*}$ and $S'_{\pi\pi^*}$ states, the stimulated triplet states from $T'_{\pi\pi^*}$ ($T_1$) by the second pulse effectively transfer to $S'_{\pi\pi^*}$ states, resulting in delayed tautomer form emission. Because of the difficulty of obtaining the absolute yield of $T_2 \rightarrow S_1$ ISC without knowing the prepared concentration of the $T_1$ state, they performed experiments to measure the relative tautomer emission intensities from TSLIF for 7HIN and

![Figure 3. The proposed mechanism of the proton transfer cycle and dynamics of transient absorption and TSLIF for HBT at 77 K. Adapted from [24].](http://rsta.royalsocietypublishing.org/)}
9,10-dibromoanthracene in which the relevant parameters had been determined. Accordingly, a value of $1.1 \times 10^{-3}$ for $\Phi_{ts}$ was calculated for 7HIN in methylcyclohexane.

Although the above materials showed effective RISC from upper triplet levels, the low PL efficiencies restrict their application in FOLEDs. The low PL efficiencies of these materials may be attributed to the competitive non-radiative decay and/or ISC processes with the aid of heavy atom effects. Therefore, new materials should be developed for highly efficient emitters in FOLEDs with both effective RISC from upper triplet levels to singlet levels and high PL efficiencies.

4. The hot exciton process in electroluminescence

In electroluminescence (EL), the holes and electrons injected from the double electrodes recombine and generate excitons, and further the exciton radiation produces light [28–30]. The external quantum efficiency (EQE) of OLEDs is expressed as the following equation:

$$\eta_{\text{ext}} = \eta_{\text{rec}} \eta_{\text{PL}} \eta_{\text{out}},$$

where $\eta_{\text{rec}}$ is the charge balance factor ($\eta_{\text{rec}}$ could reach 100% only under ideal conditions), $\eta_{\text{PL}}$ is the intrinsic PL efficiency, $\eta_{\text{out}}$ is light out-coupling efficiency (approx. 20%) and $\eta_{s}$ is spin statistic factor. According to the spin statistics, the probability of forming singlet and triplet excitons is 25% and 75%, respectively, assuming the formation cross sections for singlet and triplet excitons are equal [31–34]. Phosphorescent OLEDs (POLEDs) could employ 100% excitons (including the singlet and triplet excitons) by means of enhanced ISC, and maximum EQE of over 20% has been achieved in POLEDs [35,36]. However, the high fabrication cost of POLEDs due to the utilization of rather expensive and unsustainable transition metals will critically restrict their extensive applications. Although the FOLEDs possess much lower fabrication cost, only singlet excitons (25% of the total excitons) can be used and triplet excitons decay to the ground state as non-radiative transition [37,38]. As a result, the maximum EQE of FOLEDs is limited to 5%.

Recently, overcoming the limit of $\eta_{s}$ in FOLEDs from triplet exciton RISC process has attracted increasing attention. Adachi’s group at Kyushu University has made significant progress in this field by the design of the promising TADF materials [39–43]. $T_1$ excitons of TADF emitters could be converted into $S_1$ excitons under thermal activation because of the very small singlet–triplet energy splitting $\Delta E_{ST}$ (less than or equal to 100 meV), and $\eta_{s}$ is further drastically increased. So far, employing nearly 100% excitons has been realized in some TADF FOLEDs, and their maximum EQE is comparable to that of POLEDs. Nevertheless, the efficiencies of most TADF devices suffer from a serious roll-off at high current density, which is probably due to the long lifetime of triplet exciton or bimolecular quenching. TTA is another approach to harvest the triplet excitons in FOLEDs [44–46]. As two triplet excitons fuse and form one singlet exciton in the TTA process, $\eta_{s}$ can be increased only up to 62.5%, which will restrict the prospective applications of the TTA principle. Therefore, innovative approaches are still urgently required for the rapid development of the organic EL field.

In principle, it is feasible to increase $\eta_{s}$ through RISC from high-lying triplet exciton (hot exciton process). Recently, we developed a series of highly efficient fluorescent materials (figure 4) according to the hot exciton principle, and $\eta_{s}$ of the FOLEDs based on these emitters greatly broke through the theoretical limit of singlet excitons [7,8,33,34]. Particularly, employing approximately 100% excitons was obtained in a device of TPA-NZP [7,8]. Several distinct features in the excited state energy levels of these materials render the potential hot exciton RISC pathway, as shown in figure 5 [47]. In the case of TPA-NZP, firstly, a very large energy gap ($\Delta E_{ST} = 1.22$ eV) emerged between $S_1$ and $T_1$, which indicated the TADF process (RISC from $T_1$ to $S_1$) was impossible to occur. Alternatively, it can be found that both $S_2$ and $T_2$ belonged to a charge-transfer (CT) state, and a very small singlet–triplet energy splitting ($\Delta E_{ST} = 0.29$ eV) existed between them. Due to the fact that CT exciton possesses weak binding energy, correspondingly the spin flip between singlet state and triplet state is prone to occur for the CT excitons. The combination of the CT character of $S_2$ and $T_2$ and their identical energy level could provide an effective
RISC channel from $T_2$ to $S_2$. More importantly, as a guarantee, the $T_1$ and $T_2$ states exhibited sufficient separation in energy (1.63 eV), which results in a relatively low IC rate ($k_{IC}$) from $T_2$ to $T_1$ according to the energy gap law. Thus, in the case of TPA-NZP, it is possible that $k_{RISC}$ ($T_2 \rightarrow S_2$) is more competitive than $k_{IC}$ ($T_2 \rightarrow T_1$) due to its unique excited state properties. In the EL process of TPA-NZP, triplet excitons could be effectively converted into singlet excitons along the hot exciton channel as shown in figure 6, and as a result, using nearly all the excitons is realized in a TPA-NZP device.

Moreover, we can deduce that the unique excited state structures of hot exciton materials are crucial to their high $\eta_s$ on the basis of the comparison between TPA-QAP and TPA-AC [7,8]. Both TPA-QAP and TPA-AC exhibit green emission, and they have quite similar highest occupied molecular orbital and lowest unoccupied molecular orbital levels determined from electrochemical measurements, which implies that the carrier injection and transport properties are nearly identical for these two molecules. Nevertheless, significantly different $\eta_s$ was obtained for TPA-QAP and TPA-AC, and the corresponding values were 19% and 46%, respectively. As shown in figure 7, for TPA-QAP, closely spaced arrangement was presented in the singlet and
triplet energy levels. According to Kasha’s rule [2], the hot excitons will rapidly decay to the lowest excited states through IC relaxation. However, TADF cannot proceed in TPA-QAP due to the large energy gap (0.75 eV) between $S_1$ and $T_1$. As a consequence, only singlet excitons could be employed in a TPA-QAP device, and $\eta_s$ obeys the spin statistics ($\eta_s < 25\%$). Differently, a large energy gap (1.12 eV) seriously suppressed $k_{IC}$ from $T_2$ to $T_1$ in the case of TPA-AC. The $T_2 \rightarrow S_1$ hot exciton channel could provide a more competitive $k_{RISC}$ than $k_{IC}$ due to the close energy levels and the CT-type excited states. Thus, the abnormally high $\eta_s$ of 46% in a TPA-AC device could be attributed to the unique excited state structures similar to that in TPA-NZP. The different $T_2/T_1$ energy gaps for TPA-QAP and TPA-AC could be estimated from the different phosphorescence properties. At 77 K, TPA-QAP in methyltetrahydrofuran solutions exhibited strong phosphorescence with the emission peak at 560 nm. Nevertheless, the phosphorescence of TPA-AC cannot be observed even after much effort. The reason could be ascribed to that the high-lying triplet excitons can hardly populate the $T_1$ state due to the blocking from the large $T_2$–$T_1$ energy gap. For TPA-QAP with a small $T_2/T_1$ energy gap, when it was excited to the $S_1$ or a higher singlet state, the excitons in the $S_1$ state can relax to the $T_1$ state through a multistep process, including an ISC process from $S_1$ to a close-lying higher triplet state ($T_m$), followed with an IC process to the lowest $T_1$ state, finally the phosphorescence being emitted. Whereas in TPA-AC with large $T_2/T_1$ energy gaps, the excitons at the $S_1$ state can transfer to a close-lying higher triplet state but cannot efficiently relax down to the $T_1$ state due to the large $T_2/T_1$ energy gaps, which results in more competitive RISC ($T_2 \rightarrow S_1$) than IC ($T_2 \rightarrow T_1$). Thus no phosphorescence was observed in TPA-AC.

We have been trying various measurements to explore the RISC process in the EL of hot exciton materials. First, magneto-electroluminescence (MEL) response experiments were carried out [48]. It is well known that when the interactions between electrons and holes (the spin–spin interaction and exchange interaction) are weak (small $\Delta E_{ST}$), the singlet $| \uparrow \downarrow - \downarrow \uparrow \rangle$ and three triplet sub-states $| \uparrow \uparrow \rangle$, $| \uparrow \downarrow + \downarrow \uparrow \rangle$ and $| \downarrow \downarrow \rangle$ are degenerate, i.e. they are spin mixed, and their mixing rate depends...
Figure 7. (a) The energy levels of the first five singlet and triplet excited states in TPA-QAP and TPA-AC; (b) the exciton decay process after hole–electron recombination in OLEDs based on TPA-QAP and TPA-AC. (Online version in colour.)

on the hyperfine field that is intrinsic to organic materials, of several millitesla. In this case, all the three triplet sub-states are involved in the RISC [49]. When an external magnetic field (higher than the hyperfine field) is introduced, the degeneracy of the sub-states of the triplets is removed. As a result, spin mixing only occurs between the $|\uparrow\downarrow - \downarrow\uparrow\rangle$ and $|\uparrow\downarrow + \downarrow\uparrow\rangle$ states. Therefore, the conversion rate will be decreased, which causes a negative MEL. We have measured the MEL of TPA-NZP-based doping and non-doping devices: they both showed a rapid decrease with an increase of magnetic field in the range of the hyperfine field. These negative magnetic field effects implied that RISC indeed occurred in the TPA-NZP-based OLED. In addition, the transient PL spectrum of TPA-NZP neat film was measured with that of 5 wt% 4CzTPN-Ph : mCP (a red TADF emitter) co-deposited film as comparison shown in figure 8. The transient PL spectrum of 5 wt% 4CzTPN-Ph : mCP co-deposited film exhibited two-component decays, including the prompt decay (9.2 ns) and TADF decay (1.05 µs). As a contrast, only a short lifetime (12.2 ns) was observed for the TPA-NZP film, and there was no delayed fluorescence phenomenon. On the other hand, transient EL decay (figure 9) displayed a consistent trend with the PL decay. When electric voltage pulse was off, in the short-time range (0–0.5 µs), the EL delay was mainly dependent on the radiative decay of excitons formed before the voltage off. In this range, the long-time delayed decay was observed in 4CzTPN-Ph-based device, while only a sharp decay curve in TPA-NZP device. So we supposed that the different PL and EL decay behaviour between
TPA-NZP and 4CzTPN-Ph may originate from the different mechanisms of triplet harvesting. For the TADF emitter 4CzTPN-Ph, the delayed fluorescence could be attributed to the relatively low $k_{RISC}$ and long lifetime of $T_1$ excitons. In the case of TPA-NZP, due to the triplet excitons being harvested along the high-lying energy levels, $k_{RISC}$ could be possibly close to or even larger than the radiative rate according to Kasha’s rule, and it is reasonable that no delayed fluorescence was observed in both PL and EL processes. In fact, the large $k_{RISC}$ of the hot exciton materials facilitates the enhancement of device stability, which is a critical evaluation for the OLED performance. So it is convincing that in TPA-NZP device, the high EQE of 1.7% and 1.6% was still maintained at the brightness of 100 and 1000 cd m$^{-2}$, respectively, which were among the best results in non-doped deep-red OLEDs.

5. The design principle for the $S_1$ state of hot exciton materials

As mentioned above, high-performance OLEDs should take account of several factors, such as $\eta_s$, $\eta_{PL}$ and $\eta_{REC}$. Traditional hot exciton materials can be hardly applied in the organic EL field, due to their low PL efficiencies and poor carrier injection and transport properties. To solve these problems, donor–acceptor structures with favourable bipolar transport properties are involved in our molecules. More importantly, we made significant efforts to adjust the nature of excited $S_1$
state for the donor–acceptor molecules. In general, the excited states in organic molecular systems can be classified into two categories considering the binding energy: the CT state and local excited (LE) state \([50,51]\). The relatively weak binding energy of CT state benefits the spin mixing between singlet state and triplet state, and further affords the possibility to realize RISC \([52]\). Nevertheless, the molecules based on CT state always show low radiative transition rate and poor PL efficiency, which is mainly caused by the spatially separated transition orbital of CT state. On the contrary, the LE state with strong binding energy possesses a high radiative transition rate because of the large overlap between the transition orbitals. However, the LE type molecules usually only use the singlet excitons and cannot exceed the spin statistics. Thus, we proposed the HLCT state to combine the weak binding energy of CT state and large radiative transition rate of LE state \([7,8]\).

According to the state-mixing principle in quantum chemistry (equations (5.1) and (5.2)), state mixing can be described as a linear combination of two states of \(\psi(CT)\) and \(\psi(LE)\), and the degree of mixing of the two states is related to the mixing coefficient \(\lambda\) \([53]\). Two important factors determine \(\lambda\): (i) the energy gap \((E_{CT} - E_{LE})\) between the two states at the initial configurations, which is inversely proportional to \(\lambda\); that is to say, the smaller the energy gap, the larger the mixing coefficient and (ii) the magnitude of the coupling matrix element between these two states, which is directly proportional to \(\lambda\), and depends on the spatial wave function overlap of two states, symmetry properties and the nature of \(H\) (the electronic molecular Hamiltonian).

\[
\psi(S_1) = \psi(LE) + \lambda \times \psi(CT) \tag{5.1}
\]

and

\[
\lambda = \frac{\langle \psi_{LE} | H | \psi_{CT} \rangle}{E_{CT} - E_{LE}}. \tag{5.2}
\]

Therefore, in principle, the HLCT state could form on the condition that there is a small energy gap between LE state and CT state and a certain interstate coupling, as shown in figure 10. Recently, we achieved a series of donor–acceptor molecules with HLCT state after the careful manipulation of the distance, torsion angle and strength between the donor and acceptor moieties \([7,8,33,34,47,54,55]\). The quantified natural transition orbital (NTO) analysis indicated that the holes and particles of such molecules always exhibited obvious orbital separation and certain orbital overlap simultaneously. In experiment, the PL spectra usually displayed a large red-shift with increasing solvent polarity, while the HLCT state could ensure a relatively high PL efficiency.

For example, PTZ-BZP in figure 11 is a donor–acceptor molecule with HLCT state in \(S_1\) state \([33,34]\). The non-doped PTZ-BZP film exhibited a near-infrared emission with a peak at 700 nm, and a remarkable quantum efficiency of 16% was observed. The hole and particle NTOs of the \(S_1\) state showed an excellent balance between spatial separation and orbital overlap, indicating the coexistence of CT and LE components, which are consistent with the description of HLCT state. The fluorescence spectra become broadened and with a remarkable red-shift as the polarity

**Figure 10.** Illustration of the three possible cases of the LE and CT state energy levels in donor–acceptor molecules: (a, b) independent energy levels for their large energy gaps, and (c) possible state mixing for the small energy gap between the LE and CT states. (Online version in colour.)
of the solvent increased: from 590 nm in non-polar hexane to 790 nm in polar dichloromethane. With an increase of the solvent polarity, the Stokes shift versus the orientation polarizability plot shows two sets of linearity, which represent two different excited states in low- and high-polarity solvents, respectively. The dipole moment is calculated as 13.2 D and 31.1 D for low- and high-polarity solvents (figure 12), respectively. In high-polarity solvents, it is clear that CT state is dominant due to the large dipole moment (31.1 D) and the PL efficiency decreased rapidly as the solvent polarity increased (from 0.31 in isopropyl to 0.02 in dichloromethane). By contrast, the fluorescence behaviour could combine the relatively high PL efficiency (between 0.47 in hexane and 0.31 in isopropyl) and certain dipole moment (13.2 D) in low-polarity solvents. The HLCT character of PTZ-BZP is responsible for the unique PL properties.

Some high-performance non-doped OLEDs were fabricated using hot exciton materials as emitter based on HLCT state [7,8,33,34]. The EL emission of the devices ranged from blue to near-infrared. The detailed data are summarized in table 1. The TPA-NZP-based device emitted a deep-red light of 664 nm with the maximum EQE of 2.8% and maximum brightness of 4574 cd m$^{-2}$. The PTZ-BZP-based device exhibited the maximum EQE of 1.5% and maximum brightness of 780 cd m$^{-2}$ with a near-infrared EL emission peaked at 692 nm. A maximum EQE of 3.0% and brightness of 10 079 cd m$^{-2}$ were observed for the non-doped blue OLED based on TPA-AN. Green and orange devices showed better performance compared with red and
Table 1. The EL performance summary of the OLEDs based on hot exciton materials.

<table>
<thead>
<tr>
<th>device</th>
<th>$L_{\text{max}}$ (cd A$^{-1}$)</th>
<th>$\eta_{\text{ext}}$ (%)</th>
<th>$L_{\text{max}}$ (cd m$^{-2}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\eta_{s}$ (%)</th>
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<td>3.0</td>
<td>10 079</td>
<td>460</td>
<td>30</td>
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<td>3.2</td>
<td>13 760</td>
<td>504</td>
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<td>3.8</td>
<td>37 911</td>
<td>588</td>
<td>42</td>
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<td>664</td>
<td>93</td>
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<td>780</td>
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blue devices. The devices of TPA-AC and TPA-BZP displayed EQE of 3.2% and 3.8%, and corresponding EL emission peak located at 504 and 588 nm, respectively. The performances of the devices were among the best results of each non-doped OLEDs, and the $\eta_{s}$ of all the molecules have broken through the spin statistics limit. The favourable device performance suggested hot exciton RISC and HLCT state provided a new way to design the next-generation OLEDs.

6. Conclusion

In summary, we reviewed the basic mechanism of the hot exciton RISC process, the early materials with such unique photophysical phenomenon, and the further design of hot exciton materials for promising application in FOLEDs. Different from E- and P-type delayed fluorescence, hot exciton RISC process occurs at the high-lying energy levels, and consequently its $k_{\text{RISC}}$ could be close to or even larger than the radiative rate of $S_1$ state. On the one hand, this character facilitates avoiding the accumulation of $T_1$ excitons in EL, and further enhancing device stabilities. On the other hand, the hot exciton process is proposed to greatly increase the $\eta_{s}$ for highly efficient FOLEDs. Due to the low PL efficiency, the early materials with RISC mainly were focused on the photophysical process and barely on the FOLEDs. Here, HLCT state molecules, which achieve an incorporation of effective hot exciton RISC and high PL efficiency, are designed and used to maximize the EQE of the FOLEDs. A series of fluorescence materials based on this mechanism were developed with the EL spectra ranging from blue to near-infrared, and their excellent EQEs were harvested in the non-doped OLEDs using these materials, and their $\eta_{s}$ all broke through the upper limit of the spin statistics. HLCT state molecules with hot exciton RISC provide a new strategy to design the next-generation organic electroluminescent materials with low cost and high performance.

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