Influence of spin relaxation induced by molecular vibration on thermally activated delayed fluorescence

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ABSTRACT

Thermally activated delayed fluorescence (TADF), an effective mechanism to break the 25% statistic limit of organic light-emitting diodes (OLEDs) internal quantum efficiency, has become an active topic recently. The key to germinate TADF is the achievement of efficient reverse intersystem crossing from triplet spin state to singlet state by thermal activation, which is obviously a temperature dependence process. The direct way of thermal activation is the absorption of phonon energy, in which the transition rate from triplet state to singlet state has the Boltzmann distribution function dependence of the temperature. Nevertheless, the molecular vibration could engender spin relaxation of excitons, giving rise to different temperature dependence. This could be regarded as an indirect way of thermal activation. Here, we investigate the effect of spin relaxation caused by molecular vibration on TADF and analyze the change principles of the efficiency of TADF processes versus temperature. It is found that the experimental dependence could be well explained when the spin relaxation induced by molecular vibration is considered. Therefore, the consideration of this process helps us to understand TADF more comprehensively.

1. Introduction

Since organic light-emitting diodes (OLEDs) were constructed by Tang and VanSlyke [1] in the 1980s, these devices have aroused widespread interest and attention. Due to the unique properties of organic materials, OLEDs have great advantages and huge development space in the application of novel electronic devices [2–5]. According to the spin statistics of electron-hole pairs (excitons), the injected electrons and holes couple to form 25% singlet excitons and 75% triplet excitons in the organic light-emitting layer. The spin-forbidden of triplet excitons leads to the highest internal quantum efficiency (IQE) of only 25%. To improve OLED efficiency, it is essential to efficiently utilize the left triplet excitons for luminescence. One successful method is to use phosphorescent materials, such as Iridium (Ir) and Platinum (Pt) complexes [6,7]. In this way, one can obtain light emission from both triplet excited state and singlet excited state by increasing spin-orbit coupling so that the IQE of the devices achieves approximately 100%. However, phosphorescent materials generally use heavy metals so they are expensive and sometimes not environmental friendly. Moreover, the materials present instability problem in practical device application, particularly for the blue light [8]. Another promising attempt to break the 25% limit is to use thermally activated delayed fluorescence (TADF) [9–15] materials, which has been given stable fluorescence and high-efficiency.

In a TADF process, excitons in the low-energy triplet excited state ($T_1$) can be up-converted into the high-energy singlet excited state ($S_1$) by thermal activation and then these singlet excitons transfer to the ground state ($S_0$), which is accompanied by delayed fluorescence emission [16–18]. A direct way of thermal activation is the absorption of phonons, complementing the energy gap between the singlet and the triplet state ($\Delta E_{ST}$). Its temperature dependence is in the form of Boltzmann distribution and this process is regarded as the reverse intersystem crossing (RISC). On the other hand, temperature induces the vibration of molecules, resulting in the fluctuations of the exchange interaction of the excitons, which gives rise to spin relaxation [19]. This process engenders different temperature dependence, which can be considered as an indirect way of thermal activation. However, all present understandings on TADF are from the direct way of thermal activation, which has the Boltzmann distribution function of temperature dependence [20–23], while the indirect way of temperature due to the molecular vibration is neglected.

In this work, we suggest a model and investigate the effect of spin relaxation caused by molecular vibration on TADF. The temperature dependence of the efficiency with spin relaxation is calculated and the result is compared with present one without spin relaxation.

2. Model

The principle of TADF is schematically shown in Fig. 1. There are...
In TADF molecules, two different mechanisms in the process of TADF, which are the prompt fluorescence (PF) and the delayed fluorescence (DF). In the prompt fluorescence mechanism, excitons in the S1 state directly transmit to the S0 state by radiation (kS). Whereas in the delayed fluorescence mechanism, excitons in the S1 state have a reverse transition to the T1 state and then decay into the S0 state, which emits delayed fluorescence. These are two channels for the transition from T1 to S1 (T1 → S1). The direct transition channel is the RISC and is represented by kRISC. And the indirect transition channel is spin relaxation and is expressed by kknr. Apart from these processes, there are also the transitions from the S1 state to T1 state via the intersystem crossing (ISC) process (kISC), the spin relaxation from the S1 state to T1 state (kISC) and the non-radiative decay process from the S1 state to T1 state (kknr and kknr), respectively. In view of the energy chart exhibits in Fig. 1, the temperature dependence of TADF can be described in Equations (1) and (2).

\[
\frac{d[S_1]}{dt} = -(k_S + k_{DF} + k_{ISC} + k_P)[S_1] + (k_{RISC} + k_a)[T_1]
\]

(1)

\[
\frac{d[T_1]}{dt} = -(k_{DF} + k_{RISC} + k_a)[T_1] + (k_{ISC} + k_T)[S_1]
\]

(2)

The solution of the above differential equations is in a double exponential form:

\[ [S_1] = C_1 \exp(k_{PF} t) + C_2 \exp(k_{DF} t) \]

(3)

where C1 and C2 are proportionality coefficients for prompt and delayed fluorescence component rate and they are determined by the initial conditions. kPF and kDF indicate the prompt and delayed fluorescence component rates, respectively, which can be expressed as:

\[ k_{PF}, k_{DF} = \frac{k_S + k_{DF} + k_{ISC} + k_P + k_{RISC} + k_a}{2} \times \left( 1 \pm \sqrt{1 - \frac{4(k_S + k_{DF} + k_{ISC} + k_P)(k_{RISC} + k_a)}{(k_T + k_{DF} + k_{ISC} + k_P + k_{RISC} + k_a)^2}} \right) \]

(4)

where for kPF we take the “+”, and for kDF we take the “−”.

When the values of kS, kS, kISC and kP are larger than those of kT, kDF and kP, the values of kPF and kDF can be approximately written as follows:

\[ k_{PF} = k_S + k_{DF} + k_{ISC} + k_P \]

(5)

\[ k_{DF} = k_{DF} + \left( 1 - \frac{k_{ISC} + k_P}{k_T + k_{DF} + k_{ISC} + k_P + k_{RISC} + k_a} \right)(k_{RISC} + k_a) \]

(6)

To describe the photoluminescence quantum yield (PLQY) of the prompt fluorescence and the delayed fluorescence components, we define the prompt and the delayed components PLQY (ΦPF and ΦDF), which can be represented as:

\[ \Phi_{PF} = \frac{k'_S}{k'_S + k'_{DF} + k'_{ISC} + k'_P} = \frac{k_S}{k_P} \]

(7)

\[ \Phi_{DF} = \sum_{k=1}^n (\Phi_{ISC})_{RISC} \Phi_{PF} = \frac{\Phi_{ISC} \Phi_{RISC}}{1 - \Phi_{ISC} \Phi_{RISC}} \Phi_{PF} \]

(8)

where \( \Phi_{ISC} \) indicates the efficiency of ISC with spin relaxation from singlet to triplet states and \( \Phi_{RISC} \) the efficiency of RISC with spin relaxation from triplet to singlet states. They are given by the following formulas:

\[ \Phi_{ISC} = \frac{k_{RISC} + k_T}{k_{RISC} + k_{ISC} + k_P + k_a} \]

(9)

\[ \Phi_{RISC} = \frac{k_{RISC} + k_a}{k_{RISC} + k_{ISC} + k_P + k_a} \]

(10)

It has been known that temperature affects the spin relaxation. The spin relaxation time between singlet and triplet state is inversely proportional to the square of temperature [19]. Correspondingly, the transition rate \( k_T \) and \( k_P \) can be written by the following formulas:

\[ k_a = k_{ao} T^2 \]

(14)

\[ k_P = k_{po} T^2 \]

(15)

where \( k_{ao} \) and \( k_{po} \) are the constants that are independent of temperature.
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