



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 (ΔE_{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

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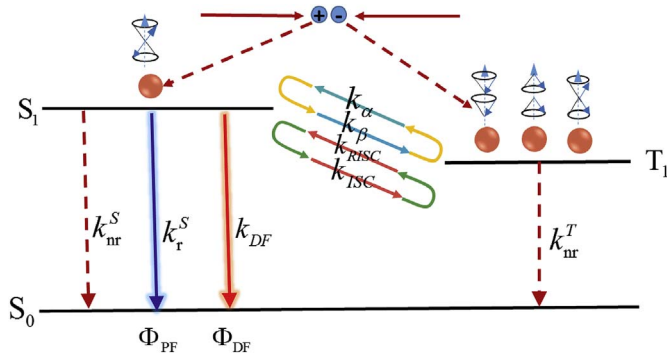


Fig. 1. Electroluminescence process in TADF molecules. Electrons and holes are injected from two electrodes, respectively, and then they encounter and form excitons. k_r^S is the radiative decay rate of S₁ and k_{DF} is the delayed fluorescence component rate; k_{nr}^S and k_{nr}^T are the non-radiative decay rate of S₁ and T₁, respectively; k_{RISC} is the RISC rate and k_{ISC} is the intersystem crossing rate; k_α is the spin relaxation rate from T₁ to S₁ and k_β is the spin relaxation rate from S₁ to T₁; Φ_{PF} and Φ_{DF} are the prompt fluorescence efficiency and delayed fluorescence efficiency, respectively.

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 directly transmit to the S₀ by radiation (k_r^S). Whereas in the delayed fluorescence mechanism, excitons in the T₁ have to be up-converted into the S₁ and then decay into the S₀, which emits delayed fluorescence. There are two channels for the transition from T₁ to S₁ (T₁ → S₁). The direct transition channel is the RISC and is represented by k_{RISC} . And the indirect transition channel is spin relaxation and is expressed by k_α . Apart from these processes, there are also the transitions from the S₁ to T₁ via the intersystem crossing (ISC) process (k_{ISC}), the spin relaxation from the S₁ to T₁ (k_β) and the non-radiative decay process from the S₁ and T₁ to S₀ (k_{nr}^S and k_{nr}^T), respectively. In view of the energy chart exhibits in Fig. 1, the principle of TADF can be described in Equations (1) and (2).

$$\frac{d[S_1]}{dt} = -(k_r^S + k_{nr}^S + k_{ISC} + k_\beta)[S_1] + (k_{RISC} + k_\alpha)[T_1] \quad (1)$$

$$\frac{d[T_1]}{dt} = -(k_{nr}^T + k_{RISC} + k_\alpha)[T_1] + (k_{ISC} + k_\beta)[S_1] \quad (2)$$

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

$$[S_1] = C_1 \exp(k_{PF}t) + C_2 \exp(k_{DF}t) \quad (3)$$

where C_1 and C_2 are proportionality coefficients for prompt and delayed fluorescence component rate and they are determined by the initial conditions. k_{PF} and k_{DF} indicate the prompt and delayed fluorescence component rates, respectively, which can be expressed as:

$$k_{PF}, k_{DF} = \frac{k_r^S + k_{nr}^S + k_{ISC} + k_\beta + k_{nr}^T + k_{RISC} + k_\alpha}{2} \times \left(1 \pm \sqrt{1 - \frac{4(k_r^S + k_{nr}^S + k_{ISC} + k_\beta)(k_{nr}^T + k_{RISC} + k_\alpha) - 4(k_{ISC} + k_\beta)(k_{RISC} + k_\alpha)}{(k_r^S + k_{nr}^S + k_{ISC} + k_\beta + k_{nr}^T + k_{RISC} + k_\alpha)^2}} \right) \quad (4)$$

where for k_{PF} we take the “+”, and for k_{DF} we take the “-”.

When the values of k_r^S , k_{nr}^S , k_{ISC} and k_β are larger than those of k_{nr}^T , k_{RISC} and k_α , the values of k_{PF} and k_{DF} can be approximately written as follows:

$$k_{PF} = k_r^S + k_{nr}^S + k_{ISC} + k_\beta \quad (5)$$

$$k_{DF} = k_{nr}^T + \left(1 - \frac{k_{ISC} + k_\beta}{k_r^S + k_{nr}^S + k_{ISC} + k_\beta} \right) (k_{RISC} + k_\alpha) \quad (6)$$

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 (Φ_{PF} and Φ_{DF}), which can be represented as:

$$\Phi_{PF} = \frac{k_r^S}{k_r^S + k_{nr}^S + k_{ISC} + k_\beta} = \frac{k_r^S}{k_{PF}} \quad (7)$$

$$\Phi_{DF} = \sum_{k=1}^{\infty} (\Phi_{ISC\beta} \Phi_{RISC\alpha})^k \Phi_{PF} = \frac{\Phi_{ISC\beta} \Phi_{RISC\alpha}}{1 - \Phi_{ISC\beta} \Phi_{RISC\alpha}} \Phi_{PF} \quad (8)$$

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

$$\Phi_{ISC\beta} = \frac{k_{ISC} + k_\beta}{k_r^S + k_{nr}^S + k_{ISC} + k_\beta} \quad (9)$$

$$\Phi_{RISC\alpha} = \frac{k_{RISC} + k_\alpha}{k_{RISC} + k_{nr}^T + k_\alpha} \quad (10)$$

In TADF process, the values of k_{RISC} , k_{nr}^S , k_{nr}^T , k_α and k_β are related to temperature. For the RISC process, high temperature could increase the rate of RISC while low temperature inhibits the process and slows the rate down. The temperature dependence of k_{RISC} can be described as a Boltzmann distribution:

$$k_{RISC} = k_{RISC1} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right) \quad (11)$$

where k_B is the Boltzmann constant, ΔE_{ST} is the singlet-triplet energy splitting, k_{RISC1} is the RISC rate that is independent of temperature and T is temperature.

We express the temperature dependence of the non-radiative decay rate of S₁ in a Boltzmann distribution [24]:

$$k_{nr}^S = k_{nr0}^S + k_{nr1}^S \exp\left(-\frac{\Delta E_{Q1}}{k_B T}\right) \quad (12)$$

where ΔE_{Q1} is the activation energy for thermal quenching from S₁. k_{nr0}^S and k_{nr1}^S are the non-radiative decay rate of S₁, k_{nr0}^S indicates the coefficient of the temperature independent item and k_{nr1}^S indicates the coefficient of the temperature dependent item, but they are independent of temperature.

From the experimental data in Ref. [25], we learn that the tendency of the non-radiative decay rate of S₁ and T₁ vary with temperature in the same way, so we also use the Boltzmann distribution to describe the dependence of non-radiative decay rate of T₁ on temperature:

$$k_{nr}^T = k_{nr0}^T + k_{nr1}^T \exp\left(-\frac{\Delta E_{Q2}}{k_B T}\right) \quad (13)$$

where ΔE_{Q2} is the activation energy for thermal quenching from T₁. k_{nr0}^T and k_{nr1}^T are the non-radiative decay rate of T₁, k_{nr0}^T indicates the coefficient of the temperature independent item and k_{nr1}^T indicates the coefficient of the temperature dependent item, but they are independent of temperature.

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_α and k_β can be written by the following formulas:

$$k_\alpha = k_{\alpha0} T^2 \quad (14)$$

$$k_\beta = k_{\beta0} T^2 \quad (15)$$

where $k_{\alpha0}$ and $k_{\beta0}$ are the constants that are independent of temperature.

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