

# Kinetic Prediction of Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence Materials

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## ABSTRACT

We demonstrate a theoretical expression that successfully reproduces rate constants of reverse intersystem crossing (RISC) ranging over five orders of magnitude in twenty different molecules exhibiting thermally activated delayed fluorescence (TADF).

## 1 Introduction

Electronic spin-flip processes in molecular excited states have attracted increasing interest for optoelectronics, photocatalytic synthesis, and biomedical applications. A relevant example is reverse intersystem crossing (RISC), the uphill transition of a non-emissive triplet excited state to an emissive singlet excited state. This process leads to E-type delayed fluorescence, also known as thermally activated delayed fluorescence (TADF), and allows an internal charge-to-photon conversion efficiency of nearly 100% in organic light-emitting diodes (OLEDs) [1]. Although materials have typically been discovered experimentally, a fundamental understanding of RISC kinetics and strategy for predicting the rate constants may open vast opportunities for theory-driven materials discovery.

RISC kinetics are often considered in the framework of Marcus theory [2]. If the spin-orbit coupling  $H_{SO}$  between the initial triplet and final singlet excited states is weak, meaning that the spin flip only occurs on the crossing seam between their potential energy surfaces (PESs), the RISC rate constant ( $k_{RISC}$ ) follows a Marcus-like non-adiabatic expression:

$$k_{RISC} = \frac{2\pi}{\hbar} |H_{SO}|^2 (4\pi\lambda k_B T)^{-1/2} \exp\left(\frac{-E_A}{k_B T}\right) \quad (1)$$

where  $\hbar$  is the reduced Planck constant,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\lambda$  is the reorganization energy, and  $E_A$  is the activation energy to reach the crossing seam. In the case of simple parabolic PESs with equal force constants, which is a crucial assumption of Marcus theory,  $E_A$  can be analytically expressed as

$$E_A = \frac{(\Delta E_{ST} + \lambda)^2}{4\lambda} \quad (2)$$

with  $\Delta E_{ST}$  as the adiabatic singlet-triplet energy difference. A key implication of Eq. 1 and Eq. 2 is that  $k_{RISC}$  can be predicted from the equilibrium geometries, which correspond to the easily computable local minima on the PESs of the initial triplet state and final singlet state. However, this understanding of RISC becomes more complicated if the spin-flip process involves an energetically higher-lying excited state as an intermediate [3-6]. Herein, we explicitly compute singlet-triplet crossing seams to quantitatively predict  $k_{RISC}$  for twenty different TADF molecules [7]. Rigorous comparisons to experimental data reported over the last decade allowed a general understanding of the RISC kinetics governed by the singlet-triplet crossing seam involving a higher-lying triplet excited state.

## 2 Experiment

Directly computing  $k_{RISC}$  from Eq. 1 requires the minimum-energy seam of the crossing (MESX), the energetically most accessible geometry on the singlet-triplet crossing seam hypersurface, as well as equilibrium geometries of the lowest-energy singlet and triplet excited states ( $S_1$  and  $T_1$ ). The singlet-triplet MESX was obtained using a composed gradient vector  $\mathbf{G}$  for the nuclear coordinates  $\mathbf{Q}$ :

$$\mathbf{G}(\mathbf{Q}) = 2(E_S(\mathbf{Q}) - E_T(\mathbf{Q})) \frac{\mathbf{v}}{|\mathbf{v}|} + \frac{1}{2} \left( \frac{\partial E_S(\mathbf{Q})}{\partial \mathbf{Q}} + \frac{\partial E_T(\mathbf{Q})}{\partial \mathbf{Q}} \right) \mathbf{P} \quad (3)$$

where

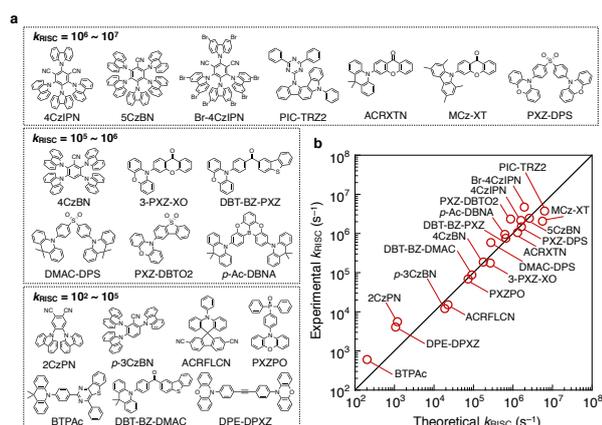
$$\mathbf{P} = 1 - \frac{\mathbf{v}\mathbf{v}^T}{|\mathbf{v}|^2} \quad (4)$$

In Eq. 3, the first term contains the difference gradient vector  $\mathbf{v}$  to minimize the square energy difference of the singlet and triplet excited states,  $(E_S - E_T)^2$ . The second term is responsible for minimizing the mean energy  $(E_S + E_T)/2$ , while the projection matrix  $\mathbf{P}$  ensures the orthogonality between the two terms of the composed gradient vector. The excited-state energy and gradient were calculated using time-dependent density functional theory (TDDFT) with the LC-BLYP functional and the 6-31+G(d) basis set within the Tamm-Dancoff approximation. The range-separated parameters for the

LC-BLYP functional were non-empirically optimized for each molecule to incorporate a reasonable amount of exact exchange.  $E_A$  was calculated as the energy difference between the MESX and the equilibrium  $T_1$ .  $\lambda$  was calculated as the difference between the  $T_1$  energies at the equilibrium  $T_1$  and  $S_1$  geometries.  $H_{SO}$  was calculated perturbatively using the Breit–Pauli spin–orbit Hamiltonian with an effective charge approximation.

### 3 Results and Discussion

For the MESX geometries of the twenty molecules shown in Fig. 1a, TDDFT predicts nonzero  $H_{SO}$  of 0.17–3.61  $\text{cm}^{-1}$  with fairly small  $E_A$  of 0.11–0.32 eV, corresponding to  $k_{RISC}$  of  $10^2$ – $10^7$   $\text{s}^{-1}$  calculated using Eq. 1 at  $T$  of 300 K. Fig. 1b compares the theoretical  $k_{RISC}$  values to the experimental values, demonstrating that the present model successfully reproduces the experimental rates. The mean absolute logarithmic error (MALE) reaches only 0.23, whereas a larger MALE of 1.2, corresponding to an error of 1.2 orders of magnitude, is observed for the values based on the conventional model using the parabolic approximation of Eq. 2. These results thus suggest the importance of the explicit computation of the singlet–triplet crossing seams for quantitatively predicting  $k_{RISC}$ .



**Fig. 1 a**, Molecular structures of the examined TADF materials categorized by their  $k_{RISC}$  values. **b**, Comparison of the experimental and theoretical  $k_{RISC}$  values.

Closer inspection of the data further reveals that  $S_1$  does not cross  $T_1$  and instead crosses the higher-lying second triplet state ( $T_2$ ) at the obtained MESX geometry. This feature explains the larger errors for the parabolic approximation, which does not account for any higher-lying excited states. We attribute the uncrossed  $S_1$  and  $T_1$  to a nonzero exchange interaction between the singlet and triplet states, which leads to  $T_1$  always lying below  $S_1$  if the two states have the same electronic configuration. In accordance with El-Sayed’s rule, a large change in the orbital angular momentum between  $S_1$  and  $T_2$  consisting of different electronic configurations induces an effective  $H_{SO}$  and thus enables spin flipping via the MESX. These

results are consistent with the RISC picture anticipated based on recent theoretical and experimental studies using ACRXTN [3] and 4CzIPN [6]. It must be stressed that  $S_1$ – $T_2$  MESX is present in every molecule examined in this quantitative study despite their wide variety of excited-state electronic configurations, including intramolecular charge transfer (CT) states and locally excited (LE) states of  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  on either donor or acceptor units, illustrating the generality of RISC via  $S_1$ – $T_2$  crossing in organic donor–acceptor molecules.

### 4 Conclusions

We have presented a RISC kinetic model that successfully predicts the experimental rates for a wide variety of organic TADF molecules. Our results suggest that explicitly computing the crossing seam between the singlet and triplet excited states leads to more reliable predictions than those obtained by the conventional approach using the Marcus parabolic approximation because the RISC in these molecules involves higher-lying triplet excited states. The presented model is thus a viable tool for theory-driven materials discovery.

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