Exact rate equations for TADF kinetic analysis

Youichi Tsuchiya
OPERA, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan.
email: tsuchiya@opera.kyushu-u.ac.jp

Keywords: thermally activated delayed fluorescence, kinetic analysis, exact rate equations

Abstract
The photophysical kinetic analysis of thermally activated delayed fluorescence (TADF) is important to quantitative evaluation for its spin-flipping process of forward and reverse intersystem crossing (ISC and RISC). Since the phenomenon of TADF was proposed in 1929,[1] many researchers try to understand its photophysics. After clarified TADF is very useful to achieve the high efficiency organic light emitting diodes in 2012,[2] the understanding of TADF mechanism become much more important. Unfavorably, over 10 analysis models have been reported for TADF on three-state system of $S_0$, $S_1$ and $T_1$, which based on different assumptions and approximations, and we have been often faced with the problem of which kinetic model should be used for newly developed TADF materials. The typical assumption is one of nonradiative rate for $S_1$ or $T_1$ ($k_{nr}^S$ or $k_{nr}^T$) is zero.[3,4] When this assumption was used, the equation should be used only for highly emissive TADF materials. However, low emissive materials also have been analyze employing these equations, because there is no report of adequate equations them. In addition, there is a problem which assumption should be applied to estimate the ISC rate. Further, this situation makes difficult to compare the reported rate constants.

In this presentation, I will explain the detail of our recent report of kinetic analysis for TADF materials on three-state system to resolve above situations.[5] To understand the TADF photophysics, it is important to understand the equation of emission decay curve, and separate to the fractions of prompt and delayed emission by the fitting curve, correctly. To reduce the assumption deriving the rate equations, the steady-state approximation (SSA) was efficient. While the assumption of $k^S \gg k_{RISC}$ is necessary to apply SSA, this should be allowed in most of the cases on the three-state system because $k_{ISC}$ included to $k^S$ is always larger than $k_{RISC}$ because the relation of exo- and endo-thermic process. Eventually, we obtained the same rate equations with two reported kinetic models mostly used; that was derived with practically no assumption with the limit condition of $k_{nr}^S = 0$ and $k_{nr}^T = 0$. These two limit conditions are providing the possible range of each rate constants. The difference of $k_{RISC}$ value for each limit condition depends the prompt and delayed emission ratio and PLQY. The exact photophysical kinetic equation set including $k_{ISC}$ for three-state system can be derived from the exact equations of emission decay and prompt /delayed emission efficiency, but it requires the numerical analysis. When we can approximate no phosphorescent in the delayed emission, the equation set becomes very simple and it provides $k_{nr}^T = 0$ as not assumption or limit condition. As a result, equation for $k_{RISC}$ became same as Dias’ model, however the equation of $k_{ISC}$ was not same. In any case, it is important to show the possible range of rate constants because $k_{nr}^T = 0$ should not be in the actual case. We are providing an excel spreadsheet to make easy the photophysical kinetic analysis.[6]

References
[6] https://doi.org/10.17630/814616e4-c5e9-44d3-8daa-cf7f2cc2d783