

## *Supporting Information*

### **Exact Solution of Kinetic Analysis for Thermally Activated Delayed Fluorescence Materials**

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## 1. Summary of the methods to estimate $k_{RISC}$ (Table S1)

Entry	Equations	Assumptions	Comments
1 <sup>5</sup>	$k_{RISC} = \frac{1}{3} k_{ISC} \exp\left(\frac{-\Delta E_{ST}}{RT}\right)$	<ul style="list-style-type: none"> <li><math>\Phi_{ISC} \approx 1</math></li> <li><math>(\Phi_p \ll \Phi_d, k_{nr}^S \approx 0)</math></li> <li><math>k_{ISC} \gg k_r^S</math></li> <li><math>k_{RISC} \gg k_r^T + k_{nr}^T</math></li> </ul>	For metal complexes.
2 <sup>6</sup>	$k_{TADF} = \frac{1}{3} k_r^S \exp\left(\frac{-\Delta E_{ST}}{RT}\right)$	<ul style="list-style-type: none"> <li><math>\Phi_{PLQY} \approx 1</math></li> <li><math>(k_{nr}^S \approx 0, k_{nr}^T \approx 0)</math></li> <li><math>\Phi_p &lt; \Phi_d, (k_{ISC} \gg k_r^S)</math></li> <li><math>\tau_d &gt; 1 \mu s</math></li> <li><math>0.05 \text{ eV} &lt; \Delta E_{ST} &lt; 0.3 \text{ eV}</math></li> <li><math>(k_r^T \approx 0)</math></li> </ul>	$k_{TADF}$ is a triplet decay rate via $S_1$ including ISC/RISC cycles.
3 <sup>7</sup>	$k_{RISC} = \frac{k_p k_d}{k_{ISC}} \cdot \frac{\Phi_d}{\Phi_p} = k_d \frac{\Phi_d}{\Phi_p \Phi_{ISC}}$	<ul style="list-style-type: none"> <li><math>k_r^S, k_{nr}^S, k_{ISC} \gg k_{RISC}, k_{nr}^T</math></li> <li><math>k_r^T \approx 0</math></li> </ul>	
4 <sup>8</sup>	$k_{RISC} = \frac{k_p k_d}{k_{ISC}} \cdot \frac{\Phi_d}{\Phi_p} = k_d \frac{\Phi_d}{\Phi_p \Phi_{ISC}}$	<ul style="list-style-type: none"> <li><math>k_r^S, k_{ISC} \gg k_{RISC}, k_{nr}^T</math></li> <li><math>k_{nr}^S \approx 0</math></li> <li><math>k_r^T \approx 0</math></li> </ul>	Transient PL prompt must be temperature independent.
5 <sup>9</sup>	$k_{RISC} \approx \frac{k_p k_d}{k_p - k_{ISC}} \approx \frac{k_p k_d}{k_r^S}$	<ul style="list-style-type: none"> <li><math>k_r^S \gg k_{nr}^S, k_r^T, k_{nr}^T</math></li> <li><math>k_{RISC} \gg k_r^T, k_{nr}^T</math></li> </ul>	
6 <sup>10</sup>	$(1) \quad k_{RISC} = \frac{k_p k_d}{k_{ISC}} \cdot \frac{\Phi_d}{\Phi_p}$ $(2) \quad k_{RISC} = \frac{k_p k_d}{k_r^S} \Phi_{PLQY}$	<ul style="list-style-type: none"> <li><math>k_p \gg k_d, k_r^T \approx 0</math></li> <li><math>(k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC} + k_{nr}^T)</math></li> <li><math>k_{nr}^S \approx 0, \Phi_{PLQY} \geq 0.9</math> for (1)</li> <li><math>k_{nr}^T \approx 0</math> for (2)</li> </ul>	$k_{RISC}$ can be determined even when $k_r^S < k_{RISC}$ .
7 <sup>11</sup>	$k_{RISC} = k_d \frac{1}{1 - \Phi_{ISC}} = k_d \frac{\Phi_p + \Phi_d}{\Phi_p}$	<ul style="list-style-type: none"> <li><math>k_{nr}^T \approx 0</math></li> <li><math>k_r^T \approx 0</math></li> <li><math>k_{ISC} \gg k_r^S \gg k_{nr}^S</math></li> <li><math>k_{ISC} \gg k_{RISC}</math></li> <li><math>\Phi_d / \Phi_p \geq 4</math></li> </ul>	
8 <sup>12</sup>	$k_{RISC} = \frac{k_p + k_d}{2} - \sqrt{\left(\frac{k_p + k_d}{2}\right)^2 - k_p k_d \left(1 + \frac{\Phi_d}{\Phi_p}\right)}$	<ul style="list-style-type: none"> <li><math>k_{nr}^T \approx 0</math></li> <li><math>k_r^T \approx 0</math></li> </ul>	$k_{RISC}$ can be determined even when $k_r^S < k_{RISC}$ .
9 <sup>13</sup>	$\frac{d[S_1]}{dt} = -(k_r^S + k_{ISC})[S_1] + k_{RISC}[T_1]$ $\frac{d[T_1]}{dt} = k_{ISC}[S_1] - k_{RISC}[T_1]$	<ul style="list-style-type: none"> <li><math>\Phi_{PLQY} \approx 1</math></li> <li><math>(k_{nr}^S \approx 0, k_{nr}^T \approx 0)</math></li> <li><math>k_r^T \approx 0</math></li> </ul>	Estimated by multi-parameter fitting.
10 <sup>14</sup>	$k_{RISC} = \frac{k_{d0}^2 - k_{p0} k_{d0}}{k_{ISC} + k_{d0} - k_{p0}}$	<ul style="list-style-type: none"> <li><math>k_{nr}^T \approx 0</math></li> <li><math>k_r^T \approx 0</math></li> </ul>	Prepare the pristine and quencher doped film. $k_{p0}$ and $k_{d0}$ are prompt and delayed decay rate of pristine film. $k_{ISC}$ is estimated by curve fitting of delayed emission for quencher doped film. Other parameters such as exciton diffusion coefficients and length are also estimated.
11 <sup>15</sup>	$k_{RISC} = k_T \Phi_{TADF}$		$k_T$ is triplet lifetime from transient absorption spectra. $\Phi_{TADF}$ is the difference of PLQY presence and absence of $O_2$ . $k_{RISC}$ is estimated as not an elementary rate but an effective rate which should be written as $k_{TADF}$ , because ISC/RISC cycle is not considered.

Reference numbers is corresponding to that in main text.

## 2. Summary of the methods to estimate $\Phi_{ISC}$ (Table S2)

Entry	Equations	Assumptions	Comments
1 <sup>16</sup>	$\Phi_{ISC} = \frac{\rho(\lambda)_{SS} k_d}{\varepsilon_T(\lambda) I_a l}$	<ul style="list-style-type: none"> <li>• Depending on estimation method of <math>\varepsilon_T(\lambda)</math><sup>16</sup></li> </ul>	
2 <sup>18</sup>	$\ln \left[ \frac{I_{PF}}{I_{DF}} - \left( \frac{1}{\Phi_{ISC}} - 1 \right) \right] = \frac{\Delta E_{ST}}{R} \cdot \frac{1}{T} + \ln \left( \frac{k_r^T + k_{nr}^T}{k_{RISC}} \right)$	<ul style="list-style-type: none"> <li>• <math>k_r^T + k_{nr}^T</math> and <math>\Phi_{ISC}</math> are temperature independent</li> </ul>	<p>Temperature dependency of the ratio of prompt and delayed emission are measured to provide the plot by using equation.</p> <p>Then, you can find a best <math>\Phi_{ISC}</math> value to obtain linearity of plot by continuous variation of <math>\Phi_{ISC}</math>.</p>
3 <sup>19</sup>	$\tau_{DF} = \tau_{phos}^0 - \left( \frac{1}{\Phi_{ISC}} - 1 \right) \tau_{phos}^0 \frac{I_{DF}}{I_{PF}}$	<ul style="list-style-type: none"> <li>• <math>k_r^T + k_{nr}^T</math> and <math>\Phi_{ISC}</math> are temperature independent</li> </ul>	<p>When <math>\tau_{phos}^0</math> is not provided, <math>\tau_{phos}^0</math> and <math>\Phi_{ISC}</math> can be obtained by the similar method of entry 2 with the temperature dependency of <math>\tau_{DF}</math> and <math>I_{DF}/I_{PF}</math>.</p>
4 <sup>7</sup>	$\Phi_{ISC} = \frac{3N}{M - N}$ $M = \Phi_{EL}^a / \Phi_{EL}^p$ $N = \Phi_{PL}^a / \Phi_{PL}^p$		<p>Only thin film state can be applied.</p> <p>The OLED device should be fabricated using same emissive layer with the thin layer for PL measurement.</p>
5 <sup>20</sup>	$\Phi_{ISC} = \frac{\Phi_{DF} + \Phi_{phos}}{\Phi_r^S + \Phi_{DF} + \Phi_{phos}} = \frac{\Phi_{DE}}{\Phi_{PLQY}}$	<ul style="list-style-type: none"> <li>• <math>k_r^S + k_{ISC} \gg k_{RISC} \gg k_r^T + k_{nr}^T</math></li> </ul>	<p>This method can be applicable to the efficient TADF emitters.</p>

Reference numbers is corresponding to that in main text.

**3. Conversion equation from quantum efficiency of prompt and delayed emission component commonly used to precise efficiency.**

The quantum efficiency of prompt and delayed emission components, which have been used commonly in most of literature, were written as,

$$\Phi_p = \frac{A_p k_d}{A_p k_d + A_d k_p} \Phi_{PLQY}, \quad (\text{S3.1})$$

$$\Phi_d = \frac{A_d k_p}{A_p k_d + A_d k_p} \Phi_{PLQY}. \quad (\text{S3.2})$$

From Eqs. 33, 34, S3.1 and S3.2 the conversion equations can be obtained as,

$$\Phi_{PF} = \Phi_p + \frac{k_d}{k_p} \Phi_d, \quad (\text{S3.3})$$

$$\Phi_{DE} = \left(1 - \frac{k_d}{k_p}\right) \Phi_d, \quad (\text{S3.4})$$

**4. Validity of  $k^S \approx k_p$  by assuming of  $k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC}$**

Eq. 40 provided by the steady state approximation, which require  $k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC}$ , can be written as

$$k_d \approx k_r^T + k_{nr}^T + \left(1 - \frac{k_{ISC}}{k^S}\right) k_{RISC},$$

$$k^T - k_d \approx \frac{k_{ISC}}{k^S} k_{RISC}.$$

From the relationship of Eqs. 19 and 78, the equation can be rewritten as

$$k_p - k^S \approx \frac{k_{ISC}}{k^S} k_{RISC},$$

$$k_p k^S - k^{S^2} \approx k_{ISC} k_{RISC},$$

$$k_p k^S - k^{S^2} \approx (k_p - k^S)(k^S - k_d),$$

$$k_p k^S - k^{S^2} \approx k_p k^S - k_p k_d - k^{S^2} + k^S k_d,$$

$$k^S \approx k_p. \tag{S4.1}$$

Therefore, when  $k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC}$  is assuming, the approximation of  $k_p \approx k^S$  can be approval.

## 5. Relationship between efficiencies and overall efficiencies (approximating $k^S \approx k_p$ )

The efficiencies related to the distribution of triplet exciton can be described to Eqs. S5.1-S5.3.

$$\Phi_{RISC} = \frac{k_{RISC}}{k_{RISC} + k_r^T + k_{nr}^T}. \quad (S5.1)$$

$$\Phi_r^T = \frac{k_r^T}{k_{RISC} + k_r^T + k_{nr}^T}. \quad (S5.2)$$

$$\Phi_{nr}^T = \frac{k_{nr}^T}{k_{RISC} + k_r^T + k_{nr}^T}. \quad (S5.3)$$

The overall efficiencies related to final distribution of triplet exciton can be described to Eqs. 49-51. From these equations, the relationship between overall efficiencies and the efficiencies related to the distribution of  $T_1$  population as Eqs. S5.4-S5.6.

$$\Phi_{RISC}^{OE} = \frac{(1 - \Phi_{ISC})\Phi_{RISC}}{1 - \Phi_{ISC}\Phi_{RISC}}. \quad (S5.4)$$

$$\Phi_r^{TOE} = \frac{\Phi_r^T}{1 - \Phi_{ISC}\Phi_{RISC}}. \quad (S5.5)$$

$$\Phi_{nr}^{TOE} = \frac{\Phi_{nr}^T}{1 - \Phi_{ISC}\Phi_{RISC}}. \quad (S5.6)$$

## 6. Derivation of $\Phi_{ISC}^{nrT=0}$ for three-state analysis

From Eqs. 55-57,

$$\begin{aligned} k_{nr}^T = 0 &= k_d - (1 - \Phi_{ISC}^{nrT=0}) \frac{(\Phi_{DE} - \Phi_{Phos})}{\Phi_{PF}} \cdot \frac{k_p k_d}{k_{ISC}^{nrT=0}} - k_d \frac{\Phi_{Phos}}{\Phi_{ISC}^{nrT=0}} \\ &= 1 - \frac{\Phi_{ISC}^{nrT=0} \Phi_{Phos} - \Phi_{ISC}^{nrT=0} \Phi_{DE} + \Phi_{DE} - \Phi_{Phos} + \Phi_{PF} \Phi_{Phos}}{\Phi_{PF} \Phi_{ISC}^{nrT=0}}. \end{aligned}$$

Therefore,

$$\Phi_{ISC}^{nrT=0} = \frac{\Phi_{DE} - \Phi_{Phos}(1 - \Phi_{PF})}{\Phi_{PF} + \Phi_{DE} - \Phi_{Phos}}. \quad (S6.1)$$



## 7. Derivation of $k_{ISC}$ at the limit conditions ( $k_{ISC}^{nrS=0}$ , $k_{ISC}^{nrT=0}$ ) for three-state analysis

From Eq. 41,

$$\Phi_{ISC}^{nrS=0} = 1 - \Phi_r^S = 1 - \Phi_{PF}. \quad (S7.1)$$

From Eqs. 54 and S7.1,

$$k_{ISC}^{nrS=0} = k_p(1 - \Phi_{PF}). \quad (S7.2)$$

From Eqs. 54 and S6.1,

$$k_{ISC}^{nrT=0} = k_p \frac{\Phi_{DE} - \Phi_{Phos}(1 - \Phi_{PF})}{\Phi_{PF} + \Phi_{DE} - \Phi_{Phos}}. \quad (S7.3)$$

When  $\Phi_{Phos} \approx 0$  was employed,

$$k_{ISC}^{nrT=0} \approx k_p \frac{\Phi_{DF}}{\Phi_{PF} + \Phi_{DE}} = k_p \frac{\Phi_{DF}}{\Phi_{PLQY}}. \quad (S7.4)$$

From Eqs. S7.2 and S7.4 the exchange equation of  $k_{ISC}$  between the limit condition is provided as,

$$k_{ISC}^{nrT=0} = k_{ISC}^{nrS=0} \frac{\Phi_{DF}}{(1 - \Phi_{PF})\Phi_{PLQY}}. \quad (S7.5)$$

## 8. Derivation of $k_{RISC}$ at the limit conditions ( $k_{RISC}^{nrS=0}$ , $k_{RISC}^{nrT=0}$ ) for three-state analysis

From Eqs. 51 and 57,

$$k_{RISC} = k_d \frac{\Phi_{DE} - \Phi_{Phos}}{\Phi_{PF} \Phi_{ISC}}. \quad (S8.1)$$

From Eqs. S6.1, S7.1, and S8.1,

$$k_{RISC}^{nrS=0} = k_d \frac{\Phi_{DE} - \Phi_{Phos}}{\Phi_{PF}(1 - \Phi_{PF})}, \quad (S8.2)$$

$$k_{RISC}^{nrT=0} = k_d \frac{\Phi_{DE}(\Phi_{PF} - \Phi_{DE}) - \Phi_{Phos}(\Phi_{PF} - \Phi_{Phos})}{\Phi_{PF} \Phi_{DE} - \Phi_{PF} \Phi_{Phos}(1 + \Phi_{PF})}. \quad (S8.3)$$

When  $\Phi_{Phos} \approx 0$  was employed for simplification,

$$k_{RISC}^{nrS=0} = k_d \frac{\Phi_{DF}}{\Phi_{PF}(1 - \Phi_{PF})} = k_d \frac{\Phi_{DF}}{\Phi_{PF} \Phi_{ISC}}, \quad (S8.4)$$

$$k_{RISC}^{nrT=0} = k_d \frac{\Phi_{PF} + \Phi_{DF}}{\Phi_{PF}} = k_d \frac{\Phi_{PLQY}}{\Phi_{PF}}. \quad (S8.5)$$

Eqs. S8.4 and S8.5 are completely corresponding to the Goushi-Masui's equation and Dias' equation respectively (see Entry 3, 4, and 6 in Table S1). This means  $k_{RISC}$  values in the literatures estimated by their method with the different assumption of  $\Phi_{nr}^S = 0$  and  $\Phi_{nr}^T = 0$  can be compared by using Eq. S8.6. In this case, the efficiency values of  $\Phi_{PF}$  and  $\Phi_{DF}$  or  $\Phi_{PLQY}$  with the ratio of  $\Phi_{PF}$  and  $\Phi_{DF}$  are requested to the literature.

$$k_{RISC}^{nrT=0} = k_{RISC}^{nrS=0} \frac{(1 - \Phi_{PF}) \Phi_{PLQY}}{\Phi_{DF}}. \quad (S8.6)$$

9. Definition of  $k_{ISC}^{Avg.}$  and  $k_{RISC}^{Avg.}$

$$k_{ISC}^{Avg.} \equiv \frac{(k_{ISC}^{nrS=0} + k_{ISC}^{nrT=0})}{2} \pm \frac{(k_{ISC}^{nrS=0} - k_{ISC}^{nrT=0})}{2}. \quad (S9.1)$$

$$k_{RISC}^{Avg.} \equiv \frac{(k_{RISC}^{nrT=0} + k_{RISC}^{nrS=0})}{2} \pm \frac{(k_{RISC}^{nrT=0} - k_{RISC}^{nrS=0})}{2}. \quad (S9.2)$$

**10. Detail derivation of  $k_{ISC}^{Avg.}$  and  $k_{RISC}^{Avg.}$  for three-state analysis (approximating  $\Phi_{Phos} \approx 0$  for simplification)**

From Eqs. S6.1, S7.4, and S9.1

$$\begin{aligned}
 k_{ISC}^{Avg.} &= \frac{1}{2} \left[ k_p(1 - \Phi_{PF}) + k_p \frac{\Phi_{DF}}{\Phi_{PLQY}} \right] \pm \frac{1}{2} \left[ k_p(1 - \Phi_{PF}) - k_p \frac{\Phi_{DF}}{\Phi_{PLQY}} \right] \\
 &= \frac{k_p}{2} \cdot \frac{\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF} \pm [\Phi_{PLQY}(1 - \Phi_{PF}) - \Phi_{DF}]}{\Phi_{PLQY}} \\
 &= \frac{k_p}{2} \cdot \frac{[\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF}] \pm \Phi_{PF}(1 - \Phi_{PLQY})}{\Phi_{PLQY}}.
 \end{aligned} \tag{S10.1}$$

From Eqs. S8.4, S8.5, and S9.2,

$$\begin{aligned}
 k_{RISC}^{Avg.} &= \frac{1}{2} \left[ k_d \frac{\Phi_{PLQY}}{\Phi_{PF}} + k_d \frac{\Phi_{DF}}{\Phi_{PF}(1 - \Phi_{PF})} \right] \pm \frac{1}{2} \left[ k_d \frac{\Phi_{PLQY}}{\Phi_{PF}} - k_d \frac{\Phi_{DF}}{\Phi_{PF}(1 - \Phi_{PF})} \right] \\
 &= \frac{k_d}{2} \cdot \frac{\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF} \pm \Phi_{PF}(1 - \Phi_{PLQY})}{\Phi_{PF}(1 - \Phi_{PF})}.
 \end{aligned} \tag{S10.2}$$

Because the relationship of Eq. S7.5,  $k_{ISC}^{Ave.}$  can be obtained from reported  $k_{ISC}$  by using S10.1 as

$$k_{ISC}^{Avg.} = k_{ISC}^{nrS=0} \frac{\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF} \pm \Phi_{PF}(1 - \Phi_{PLQY})}{2\Phi_{PLQY}(1 - \Phi_{PF})}. \tag{S10.3}$$

$$k_{ISC}^{Avg.} = k_{ISC}^{nrT=0} \frac{\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF} \pm \Phi_{PF}(1 - \Phi_{PLQY})}{2\Phi_{DF}}. \tag{S10.4}$$

Because the relationship of Eq. S8.6,  $k_{RISC}^{Ave.}$  can be obtained from reported  $k_{RISC}$  by using S10.2 as

$$k_{RISC}^{Avg.} = k_{RISC}^{nrS=0} \frac{\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF} \pm \Phi_{PF}(1 + \Phi_{PLQY})}{2\Phi_{DF}}. \tag{S10.5}$$

$$k_{RISC}^{Avg.} = k_{RISC}^{nrT=0} \frac{\Phi_{PLQY}(1 - \Phi_{PF}) + \Phi_{DF} \pm \Phi_{PF}(1 - \Phi_{PLQY})}{2\Phi_{PLQY}(1 - \Phi_{PF})}. \tag{S10.6}$$

## 11. Analysis of exciton distribution of three-state system at photoexcitation

$$\begin{aligned}
1 &= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{ISC}^{OE} \\
&= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{ISC}^{OE} \left( \Phi_r^{T\ OE} + \Phi_{nr}^{T\ OE} + \Phi_{RISC}^{OE} \right) \\
&= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{ISC}^{OE} \Phi_r^{T\ OE} + \Phi_{ISC}^{OE} \Phi_{nr}^{T\ OE} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \\
&= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{phos} + \Phi_{ISC}^{OE} \Phi_{nr}^{T\ OE} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \left( \frac{\Phi_r^S + \Phi_{nr}^S}{\Phi_r^S + \Phi_{nr}^S} \right) \\
&= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{phos} + \Phi_{ISC}^{OE} \Phi_{nr}^{T\ OE} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \frac{\Phi_r^S}{\Phi_r^S + \Phi_{nr}^S} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \frac{\Phi_{nr}^S}{\Phi_r^S + \Phi_{nr}^S} \\
&= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{phos} + \Phi_{ISC}^{OE} \Phi_{nr}^{T\ OE} + \Phi_{DF} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \frac{\Phi_{nr}^S}{\Phi_r^S + \Phi_{nr}^S} \\
&= \Phi_{PF} + \Phi_{nr}^{S\ OE} + \Phi_{DE} + \Phi_{ISC}^{OE} \Phi_{nr}^{T\ OE} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \frac{\Phi_{nr}^S}{\Phi_r^S + \Phi_{nr}^S} \\
&= \Phi_{PLQY} + \Phi_{nr}^{S\ OE} + \Phi_{ISC}^{OE} \Phi_{nr}^{T\ OE} + \Phi_{ISC}^{OE} \Phi_{RISC}^{OE} \frac{\Phi_{nr}^S}{\Phi_r^S + \Phi_{nr}^S}. \tag{S11.1}
\end{aligned}$$

$\Phi_{PF}$  and overall efficiencies are the final distribution considering the ISC/RISC cycles. Therefore,  $S_1$  excitons via  $T_1$  are distributed with essential efficiencies of  $\Phi_r^S$  and  $\Phi_{nr}^S$ . The finally distributed  $S_1$  excitons via  $T_1$  ( $\Phi_{ISC}^{OE} \Phi_{RISC}^{OE}$ ) must not distribute to ISC process anymore to generate  $T_1$ . When  $k^S \approx k_p$  was employed,  $\Phi_{PF}$ ,  $\Phi_{nr}^{S\ OE}$ , and  $\Phi_{ISC}^{OE}$  can be written by  $\Phi_r^S$ ,  $\Phi_{nr}^S$ , and  $\Phi_{ISC}$ , respectively.

Note for definition of each efficiency related to  $S_1$ :

$$\begin{aligned}
\Phi_{PF} &= k_r^S/k_p, & \Phi_{nr}^{S\ OE} &= k_{nr}^S/k_p, & \Phi_{ISC}^{OE} &= (k_{ISC} + k_p - k^S)/k_p \\
\Phi_r^S &= k_r^S/k^S, & \Phi_{nr}^S &= k_{nr}^S/k^S, & \Phi_{ISC} &= k_{ISC}/k^S \\
k^S &= k_r^S + k_{nr}^S + k_{ISC}
\end{aligned}$$

## 12. Detail derivation of exact rate equation for $k_{ISC}$ (Eq. 73)

From Eqs. 70, 71, and 72, the quadratic formula of  $k_{ISC}$  was obtained as below.

$$\begin{aligned}\Phi_{DE}R_{DE}^{DF} &= \frac{k_r^S}{k^S - k_{ISC}} \Phi_{ISC}^{OE} \Phi_{RISC}^{OE}, \\ \Phi_{DE}R_{DE}^{DF}(k^S - k_{ISC}) &= k_r^S \Phi_{ISC}^{OE} \Phi_{RISC}^{OE}, \\ \Phi_{DE}R_{DE}^{DF}(k^S - k_{ISC}) &= k_r^S \frac{k_{ISC} + k_p - k^S}{k_p} \cdot \frac{k_{RISC} - k_p + k^S}{k_d}, \\ \frac{k_p k_d}{k_r^S} \Phi_{DE}R_{DE}^{DF}(k^S - k_{ISC}) &= [k_{ISC} + (k_p - k^S)][k_{RISC} - (k_p - k^S)], \\ \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF}(k^S - k_{ISC}) &= k_{ISC} k_{RISC} + (k_p - k^S) k_{RISC} - (k_p - k^S) k_{ISC} - (k_p - k^S)^2, \\ \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF}(k^S - k_{ISC}) &= (k_p - k^S)(k^S - k_d) + (k_p - k^S) k_{RISC} - (k_p - k^S) k_{ISC} - (k_p - k^S)^2, \\ (k_p - k^S) k_{ISC} - \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF} k_{ISC} &= (k_p - k^S)[k^S - k_d - (k_p + k^S)] + (k_p - k^S) k_{RISC} - \frac{\Phi_{DE}}{\Phi_{PF}} k_d k^S R_{DE}^{DF}, \\ (k_p - k^S) k_{ISC} - \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF} k_{ISC} &= (k_p - k^S)(2k^S - k_d - k_p) + (k_p - k^S) k_{RISC} - \frac{\Phi_{DE}}{\Phi_{PF}} k_d k^S R_{DE}^{DF}, \\ (k_p - k^S) k_{ISC} - \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF} k_{ISC} &= (k_p - k^S)(2k^S - k_d - k_p) + \frac{(k_p - k^S)^2 (k^S - k_d)}{k_{ISC}} - \frac{\Phi_{DE}}{\Phi_{PF}} k_d k^S R_{DE}^{DF}, \\ (k_p - k^S - \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF}) k_{ISC}^2 - \left[ (k_p - k^S)(2k^S - k_d - k_p) - \frac{\Phi_{DE}}{\Phi_{PF}} k_d k^S R_{DE}^{DF} \right] k_{ISC} &- (k_p - k^S)^2 (k^S - k_d) = 0, \\ \left( \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF} - k_p + k^S \right) k_{ISC}^2 + \left[ (k_p - k^S)(k^S - k_p - k_d) + k^S (k_p - k^S) - \frac{\Phi_{DE}}{\Phi_{PF}} k_d k^S R_{DE}^{DF} \right] k_{ISC} &+ (k_p - k^S)^2 (k^S - k_d) = 0, \\ \left( \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF} - k_p + k^S \right) k_{ISC}^2 + \left[ (k_p - k^S)(k^S - k_p - k_d) - k^S \left( \frac{\Phi_{DE}}{\Phi_{PF}} k_d R_{DE}^{DF} - k_p + k^S \right) \right] k_{ISC} &+ (k_p - k^S)^2 (k^S - k_d) = 0.\end{aligned}$$

Therefore, the solution using quadratic formula for  $k_{ISC}$  is as below.

$$k_{ISC} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}. \quad (S12.1)$$

$$a = k_d \frac{\Phi_{DE}}{\Phi_{PF}} R_{DE}^{DF} - k_p + k^S. \quad (S12.2)$$

$$b = (k_p - k^S)(k^S - k_p - k_d) - a k^S. \quad (S12.3)$$

Because  $k_{ISC}$  should be smaller than  $k^S$ , the value is uniquely determined as,

$$k_{ISC} = \frac{-b - \sqrt{b^2 - 4ac}}{2a}. \quad (S12.4)$$

### 13. Equation conversion of $k_{nr}^S$ from Eq. 83 to Eq. 85

From Eqs. 82, 83, 86, and 88,

$$\begin{aligned}
 k_{nr}^S &= k^S - k_r^S - k_{ISC} = \left( k_p - k_d \frac{\Phi_{DF}}{\Phi_{PF}} \right) - k_p \Phi_{PF} - \left( k_p \frac{\Phi_{DF}}{\Phi_{PLQY}} - k_d \frac{\Phi_{DF}}{\Phi_{PF}} \right) \\
 &= k_p \left( 1 - \Phi_{PF} - \frac{\Phi_{DF}}{\Phi_{PLQY}} \right) \\
 &= k_p \left( \frac{\Phi_{PLQY}}{\Phi_{PLQY}} - \frac{\Phi_{PF} \Phi_{PLQY}}{\Phi_{PLQY}} - \frac{\Phi_{DF}}{\Phi_{PLQY}} \right) \\
 &= k_p \left( \frac{\Phi_{PF} + \Phi_{DF} - \Phi_{PF}(\Phi_{PF} + \Phi_{DF}) - \Phi_{DF}}{\Phi_{PLQY}} \right) \\
 &= k_p \left( \frac{\Phi_{PF} - \Phi_{PF}^2 - \Phi_{PF} \Phi_{DF}}{\Phi_{PLQY}} \right) \\
 &= k_p \frac{\Phi_{PF}}{\Phi_{PLQY}} (1 - \Phi_{PF} - \Phi_{DF}) \\
 &= k_p \frac{\Phi_{PF}}{\Phi_{PLQY}} [1 - (\Phi_{PF} + \Phi_{DF})] \\
 &= k_p \frac{\Phi_{PF}}{\Phi_{PLQY}} (1 - \Phi_{PLQY}). \tag{S13.1}
 \end{aligned}$$

#### 14. Detail derivation of exact rate equation for $k^S$ (Eq. 96)

From Eqs. 81, 88, 89, and 91,

$$\begin{aligned}
k^S &= k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} + k_{ISC} \frac{\Phi_r^T}{\Phi_r^S}, \\
k^S &= k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} + k_{ISC} \frac{\frac{k_p k_d \Phi_{DE} (1 - R_{DE}^{DF})}{(k_{ISC} + k_p - k^S)(k_p + k_d - k^S)}}{\frac{k_r^S}{k^S}}, \\
&= k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} + \frac{k_{ISC} k_p k_d \Phi_{DE} (1 - R_{DE}^{DF}) k^S}{k_p \Phi_{PF} (k_{ISC} + k_p - k^S) (k_p + k_d - k^S)}, \\
&= k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} + \frac{k_{ISC} k_d \Phi_{DE} (1 - R_{DE}^{DF}) k^S}{\Phi_{PF} [k^{S^2} - (k_{ISC} + 2k_p + k_d) k^S + (k_{ISC} + k_p)(k_p + k_d)]}, \\
k^S [k^{S^2} - (k_{ISC} + 2k_p + k_d) k^S + (k_{ISC} + k_p)(k_p + k_d)] & \\
&= \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) [k^{S^2} - (k_{ISC} + 2k_p + k_d) k^S + (k_{ISC} + k_p)(k_p + k_d)] + k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} (1 - R_{DE}^{DF}) k^S, \\
k^{S^3} - (k_{ISC} + 2k_p + k_d) k^{S^2} + (k_{ISC} + k_p)(k_p + k_d) k^S & \\
&= \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^{S^2} - (k_{ISC} + 2k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^S + (k_{ISC} + k_p)(k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) \\
&\quad + k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} (1 - R_{DE}^{DF}) k^S, \\
k^{S^3} - (k_{ISC} + 2k_p + k_d) k^{S^2} - \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^{S^2} + (k_{ISC} + k_p)(k_p + k_d) k^S + (k_{ISC} + 2k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^S & \\
&\quad - k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} (1 - R_{DE}^{DF}) k^S - (k_{ISC} + k_p)(k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) = 0, \\
k^{S^3} - \left( k_{ISC} + 2k_p + k_d + k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^{S^2} + (k_{ISC} k_p + k_p^2 + k_{ISC} k_d + k_p k_d) k^S & \\
&\quad + \left( k_{ISC} k_p + 2k_p^2 + k_p k_d - k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} - 2k_p k_d \frac{\Phi_{DE}}{\Phi_{PF}} - k_d^2 \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^S - k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} (1 - R_{DE}^{DF}) k^S \\
&\quad - (k_{ISC} + k_p)(k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) = 0, \\
k^{S^3} - \left( k_{ISC} + 2k_p + k_d + k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) k^{S^2} & \\
&\quad + \left( k_{ISC} k_p + k_p^2 + k_{ISC} k_d + k_p k_d + k_{ISC} k_p + 2k_p^2 + k_p k_d - k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} - 2k_p k_d \frac{\Phi_{DE}}{\Phi_{PF}} - k_d^2 \frac{\Phi_{DE}}{\Phi_{PF}} \right. \\
&\quad \left. - k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} (1 - R_{DE}^{DF}) \right) k^S - (k_{ISC} + k_p)(k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) = 0, \\
k^{S^3} - \left[ k_{ISC} + 3k_p + k_d \left( 1 - \frac{\Phi_{DE}}{\Phi_{PF}} \right) \right] k^{S^2} & \\
&\quad + \left[ 2k_{ISC} k_p + 3k_p^2 + 2k_p k_d \left( 1 - \frac{\Phi_{DE}}{\Phi_{PF}} \right) + k_{ISC} k_d \left( 1 - \frac{\Phi_{DE}}{\Phi_{PF}} \right) - k_d^2 \frac{\Phi_{DE}}{\Phi_{PF}} - k_{ISC} k_d \frac{\Phi_{DE}}{\Phi_{PF}} (1 - R_{DE}^{DF}) \right] k^S \\
&\quad - (k_{ISC} + k_p)(k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) = 0, \\
k^{S^3} - \left[ k_{ISC} + 3k_p + k_d \left( 1 - \frac{\Phi_{DE}}{\Phi_{PF}} \right) \right] k^{S^2} & \\
&\quad - \left\{ k_p \left\{ 3k_p - 2 \left[ k_{ISC} + 3k_p + k_d \left( 1 - \frac{\Phi_{DE}}{\Phi_{PF}} \right) \right] \right\} - k_d^2 \frac{\Phi_{DE}}{\Phi_{PF}} + k_{ISC} k_d \left[ 1 - \frac{\Phi_{DE}}{\Phi_{PF}} (2 - R_{DE}^{DF}) \right] \right\} k^S \\
&\quad - (k_{ISC} + k_p)(k_p + k_d) \left( k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}} \right) = 0.
\end{aligned}$$



Therefore,

$$k^S{}^3 + dk^S{}^2 + ek^S + f = 0, \quad (\text{S14.1})$$

$$d = -\left[k_{ISC} + 3k_p + k_d \left(1 - \frac{\Phi_{DE}}{\Phi_{PF}}\right)\right], \quad (\text{S14.2})$$

$$e = k_{ISC}k_d \left[1 - \frac{\Phi_{DE}}{\Phi_{PF}}(2 - R_{DE}^{DF})\right] - k_p(3k_p + 2d) - k_d^2 \frac{\Phi_{DE}}{\Phi_{PF}}, \quad (\text{S14.3})$$

$$f = -(k_{ISC} + k_p)(k_p + k_d) \left(k_p - k_d \frac{\Phi_{DE}}{\Phi_{PF}}\right). \quad (\text{S14.4})$$

The solutions of cubic equation were obtained by Cardano–Tartaglia formula as,

$$k^S{}_1 = \sqrt[3]{-g + \sqrt{g^2 + h^3}} + \sqrt[3]{-g - \sqrt{g^2 + h^3}} - \frac{1}{3}d, \quad (\text{S14.5})$$

$$k^S{}_2 = \frac{-1 + i\sqrt{3}}{2} \times \sqrt[3]{-g + \sqrt{g^2 + h^3}} + \frac{-1 - i\sqrt{3}}{2} \times \sqrt[3]{-g - \sqrt{g^2 + h^3}} - \frac{1}{3}d, \quad (\text{S14.6})$$

$$k^S{}_3 = \frac{-1 - i\sqrt{3}}{2} \times \sqrt[3]{-g + \sqrt{g^2 + h^3}} + \frac{-1 + i\sqrt{3}}{2} \times \sqrt[3]{-g - \sqrt{g^2 + h^3}} - \frac{1}{3}d. \quad (\text{S14.7})$$

$$g = \frac{27f + 2d^3 - 9de}{54}. \quad (\text{S14.8})$$

$$h = \frac{3e - d^2}{9}. \quad (\text{S14.9})$$

Because  $k^S$  should be smaller than  $k_p$  and larger than  $k_{ISC}$  ( $k_{ISC} < k^S < k_p$ ), the solution to the cubic equation is uniquely determined as  $k^S{}_2$ .

NOTE:

The discriminant  $D$  for  $k^S{}^3 + dk^S{}^2 + ek^S + f = 0$  is written by,

$$D = -4e^3 + e^2d^2 - 4fd^3 + 18def - 27f^2$$

The solutions of cubic equation can be obtained as,

$D > 0$ : three real roots

$D < 0$ : one real root and two imaginary roots

$D = 0$ : multiple root

## 15. Detail derivation of rate constants for four-state analysis among $S_0$ , $S_1$ , $T_1$ and $T_n$

Here, we derived the rate equations for the four-state analysis considering higher triplet state ( $T_n$ ) as an intermediate state of RISC state with the generally expected assumptions for the emitters.

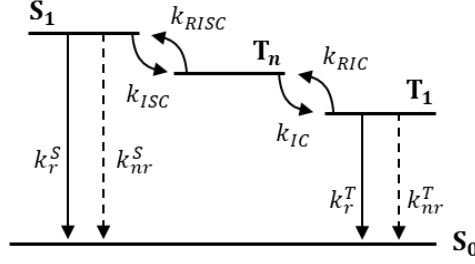


Figure S1. Schematic diagram for four-state analysis of  $S_0$ ,  $S_1$ ,  $T_1$  and  $T_n$ .

When we assume direct ISC/RISC process between  $S_1$  and  $T_1$  state and direct radiative/nonradiative process from  $T_n$  to  $S_0$  are forbidden, those decay pass can be eliminated. These assumptions should be related to the El-Saied's and Kasha's rules (Figure S1). The global decay rate from each excited state in the absence of exciton-formation processes can be formulated as

$$\frac{d[S_1]}{dt} = -k_r^S[S_1] - k_{nr}^S[S_1] - k_{ISC}[S_1] + k_{RISC}[T_n], \quad (S15.1)$$

$$\frac{d[T_n]}{dt} = -k_{RISC}[T_n] - k_{IC}[T_n] + k_{ISC}[S_1] + k_{RIC}[T_1], \quad (S15.2)$$

$$\frac{d[T_1]}{dt} = -k_r^T[T_1] - k_{nr}^T[T_1] - k_{RIC}[T_1] + k_{IC}[T_n], \quad (S15.3)$$

where  $[T_n]$  is the densities of  $T_n$  excitons,  $k_{IC}$  and  $k_{RIC}$  are the rate constants for internal conversion (IC) and reverse-internal conversion (RIC) processes. In this system, all three components of  $[S_1]$ ,  $[T_n]$ , and  $[T_1]$  should be provide as the tri-exponential curves. Therefore, the emission decay can be fit with a tri-exponential curve as,

$$I(t) = A_p \exp(-k_p t) + A_{d1} \exp(-k_{d1} t) + A_{d2} \exp(-k_{d2} t), \quad (S15.4)$$

where  $A_p$ ,  $A_{d1}$ ,  $A_{d2}$ ,  $k_p$ ,  $k_{d1}$ , and  $k_{d2}$  are the pre-exponential factors ( $A$ ) and decay rates ( $k$ ) for prompt ( $p$ ), primary delayed ( $d1$ ), and secondary delayed ( $d2$ ) components. To obtain the quantum efficiency of prompt ( $\Phi_{PF}$ ), primary delayed ( $\Phi_{DE1}$ ), and secondary ( $\Phi_{DE2}$ ) delayed components, Eq. S15.4 should be rewritten by,

$$I(t) = (A_p + A_{d1} + A_{d2}) \exp(-k_p t) + (A_{d1} + A_{d2}) [-\exp(-k_p t) + \exp(-k_{d1} t)] + A_{d2} [-\exp(-k_{d1} t) + \exp(-k_{d2} t)]. \quad (S15.5)$$

In this form, the first, second, and third terms are exactly corresponding to the prompt, primary delayed and secondary delayed components, respectively, and each efficiency can be estimated as Eqs. S15.6-S15.8,

$$\begin{aligned} \Phi_{PF} &= \frac{\frac{A_p + A_{d1} + A_{d2}}{k_p}}{\frac{A_p + A_{d1} + A_{d2}}{k_p} + \frac{A_{d1} + A_{d2}}{k_{d1}} - \frac{A_{d1} + A_{d2}}{k_p} + \frac{A_{d2}}{k_{d2}} - \frac{A_{d2}}{k_{d1}}} \Phi_{PLQY} \\ &= \frac{(A_p + A_{d1} + A_{d2})k_{d1}k_{d2}}{A_p k_{d1}k_{d2} + A_{d1}k_p k_{d2} + A_{d2}k_p k_{d1}} \Phi_{PLQY}. \end{aligned} \quad (S15.6)$$

$$\begin{aligned}
\Phi_{DE1} &= \frac{\frac{A_{d1} + A_{d2}}{k_{d1}} - \frac{A_{d1} + A_{d2}}{k_p}}{\frac{A_p + A_{d1} + A_{d2}}{k_p} + \frac{A_{d1} + A_{d2}}{k_{d1}} - \frac{A_{d1} + A_{d2}}{k_p} + \frac{A_{d2}}{k_{d2}} - \frac{A_{d2}}{k_{d1}}} \Phi_{PLQY} \\
&= \frac{(A_{d1} + A_{d2})(k_p - k_{d1})k_{d2}}{A_p k_{d1} k_{d2} + A_{d1} k_p k_{d2} + A_{d2} k_p k_{d1}} \Phi_{PLQY}.
\end{aligned} \tag{S15.7}$$

$$\begin{aligned}
\Phi_{DE2} &= \frac{\frac{A_{d2}}{k_{d2}} - \frac{A_{d2}}{k_{d1}}}{\frac{A_p + A_{d1} + A_{d2}}{k_p} + \frac{A_{d1} + A_{d2}}{k_{d1}} - \frac{A_{d1} + A_{d2}}{k_p} + \frac{A_{d2}}{k_{d2}} - \frac{A_{d2}}{k_{d1}}} \Phi_{PLQY} \\
&= \frac{A_{d2}(k_{d1} - k_{d2})k_p}{A_p k_{d1} k_{d2} + A_{d1} k_p k_{d2} + A_{d2} k_p k_{d1}} \Phi_{PLQY}.
\end{aligned} \tag{S15.8}$$

Under the assumption of  $k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC}$  with the restriction condition of  $[S_1] \gg [T_n]$  ( $t \ll 1/k_p$ ), Eq. S15.1 can be rewritten as Eq. S15.9. Therefore, the singlet decay rate ( $k^S$ ) can be approximate to the prompt decay rate ( $k_p$ ), and the function of time can be written as Eq. S15.10.

$$\frac{d[S_1]}{[S_1]} \approx (-k_r^S - k_{nr}^S - k_{ISC})dt, \tag{S15.9}$$

$$[S_1] \approx A_S \exp[-(k_r^S + k_{nr}^S + k_{ISC})t] = A_S \exp(-k^S t) \approx A_S \exp(-k_p t), \tag{S15.10}$$

where  $A_S$  is a pre-exponential factor.

Next, we focus on the exponential decay of  $[T_n]$ . Eq. S15.2 can be rewritten as Eq. S15.11 under the assumption of  $k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC}$  and  $k_{RISC} + k_{IC} \gg k_{RIC}$  with the restriction condition of  $[T_1] \ll [T_n]$  and  $[S_1] \ll [T_n]$  ( $1/k_p \ll t \ll 1/k_{d1}$ ). By the assumption of  $k_{RISC} + k_{IC} \gg k_{RIC}$ , the term related to the  $T_1$  can be vanished.

$$\frac{d[T_n]}{[T_n]} = \left( -k_{RISC} - k_{IC} + k_{ISC} \frac{[S_1]}{[T_n]} \right) dt, \tag{S15.11}$$

The time dependent term of  $[S_1]/[T_n]$  can be obtained as non-time-dependent value by the steady state approximation (SSA) of Eq. S15.1,  $d[S_1]/dt \approx 0$ .

$$\frac{[S_1]}{[T_n]} \approx \frac{k_{RISC}}{k_r^S + k_{nr}^S + k_{ISC}}. \tag{S15.12}$$

This require the assumption some of  $k_r^S$ ,  $k_{nr}^S$ , or  $k_{ISC}$  is much larger than  $k_{RISC}$ . When  $T_n$  level is lying below  $S_1$  level,  $k_{ISC} \gg k_{RISC}$  is always approved because the relationship of exo- and endothermic process. If  $k_{ISC} \gg k_{RISC}$  is satisfied as a consequence, it should not matter whether  $T_n$  level is lying above  $S_1$  level. By using Eq. S15.12, the time dependence for  $[T_n]$  is provided as Eq. S15.13.

$$\begin{aligned}
[T_n](t) &\approx A_{Tn} \exp \left\{ - \left[ \left( 1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} \right) k_{RISC} + k_{IC} \right] t \right\} \\
&= A_{Tn} \exp(-k^{Tn} t) \approx A_{Tn} \exp(-k_{d1} t),
\end{aligned} \tag{S15.13}$$

where  $A_{Tn}$  is a pre-exponential factor,  $k^{Tn}$  is a decay rate of  $T_n$  state. Therefore,  $k_{d1}$  can be approximate as,

$$k_{d1} \approx \left( 1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} \right) k_{RISC} + k_{IC}. \tag{S15.14}$$

Further, we focus on the exponential decay of  $[T_1]$ . Eq. S15.3 can be rewritten as Eq. S15.15 under the assumption of  $k_{RISC} + k_{IC} \gg k_{RIC}$  with the restriction condition of  $[T_n] \ll [T_1]$   $t \gg 1/k_{d2}$ .

$$\frac{d[T_1]}{[T_1]} = \left( -k_r^T - k_{nr}^T - k_{RIC} + k_{IC} \frac{[T_n]}{[T_1]} \right) dt. \quad (S15.15)$$

The time dependent term of  $[T_n]/[T_1]$  can be obtained as non-time-dependent value by the steady state approximation (SSA) of Eqs. S15.1 and S15.2,  $d[S_1]/dt \approx 0$  and  $d[T_n]/dt \approx 0$ , respectively; this is necessary to assume  $k_{IC} \gg k_{RIC}$  but it always approved because of the relationship of exo- and endothermic process.

$$\frac{[T_n]}{[T_1]} \approx \frac{k_{RIC}}{\left( 1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} \right) k_{RISC} + k_{IC}}. \quad (S15.16)$$

By the similar process, observed  $k_{d2}$  can be written as Eq. S15.17.

$$k_{d2} \approx k^{T1} = \left[ 1 - \frac{k_{IC}}{\left( 1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} \right) k_{RISC} + k_{IC}} \right] k_{RIC}^T + k_r^T + k_{nr}^T. \quad (S15.17)$$

The total decay efficiency of singlet excitons generated by photo-excitation is the sum of  $\Phi_r^S$  ( $\approx \Phi_{PF}$ ),  $\Phi_{nr}^S$  and  $\Phi_{ISC}$ .

$$\Phi_r^S + \Phi_{nr}^S + \Phi_{ISC} = 1. \quad (S15.18)$$

The decay efficiency of  $T_n$  excitons resulted from an ISC process is the sum of  $\Phi_{RISC}$  and the internal conversion ( $\Phi_{IC}^T$ ). It should be noted again here, we assumed that the  $T_n$  excitons do not decay directly to the  $S_0$  state but rather through the  $T_1$  state, related to Kasha's rule.

$$\Phi_{RISC} + \Phi_{IC}^T = 1. \quad (S15.19)$$

Because of  $k_r^S + k_{nr}^S + k_{ISC} \gg k_{RISC}$ , the RISC process controls the decay of  $T_n$  excitons via the  $S_1$  state and  $S_1$  excitons generated by the RISC process rapidly decayed to  $S_0$  or  $T_n$  states according to Eq. S15.18. Therefore, the multiple ISC/RISC cycle is present. In this case, the efficiencies in Eq. S15.19 should be modified by using overall efficiencies (OEs), which are the final distributed exciton ratio between  $S_1$  and  $T_n$  population via ISC/RISC cycles; those are  $\Phi_{RISC}^{OE} > \Phi_{RISC}$  and  $\Phi_{IC}^{T,OE} > \Phi_{IC}^T$ . Observed decay rate is an apparent value of  $T_n$  decays, OEs are employed to the analysis. Therefore,  $\Phi_{ISC}$  can be divided into  $\Phi_{RISC}^{OE}$  and  $\Phi_{IC}^{T,OE}$ , and the total efficiency is given by,

$$\Phi_{RISC}^{OE} + \Phi_{IC}^{T,OE} = 1. \quad (S15.20)$$

Similarly, the RIC process controls the decay of  $T_1$  excitons via the  $T_n$  state and  $T_n$  excitons generated by the RIC process rapidly decayed to  $S_1$  or  $T_1$  states according to Eq. S15.20 because of  $k_{RISC} + k_{IC} \gg k_{RIC}$ . Therefore, the multiple IC/RIC cycle is present. The efficiencies related to  $T_1$  and its OEs are written by Eqs. S15.21 and S15.22; those are  $\Phi_r^{T,OE} > \Phi_r^T$ ,  $\Phi_{nr}^{T,OE} > \Phi_{nr}^T$  and  $\Phi_{RIC}^{OE} < \Phi_{RIC}$ . Observed decay rate is an apparent value of  $T_1$  decay, OEs are employed to the analysis. Therefore,  $\Phi_{ISC}\Phi_{IC}^{OE}$  can be divided into  $\Phi_r^{T,OE}$ ,  $\Phi_{nr}^{T,OE}$  and  $\Phi_{RIC}^{OE}$ .

$$\Phi_r^T + \Phi_{nr}^T + \Phi_{RIC} = 1. \quad (S15.21)$$

$$\Phi_r^{T,OE} + \Phi_{nr}^{T,OE} + \Phi_{RIC}^{OE} = 1. \quad (S15.22)$$

The fraction of  $T_n$  exciton decay event via  $S_1$  ( $\Phi_{ISC}\Phi_{RISC}^{OE}$ ) can decay either radiatively ( $\Phi_r^S$ ) or non-radiatively ( $\Phi_{nr}^S$ ), because  $\Phi_{RISC}^{OE}$  is the finally distributed exciton ratio after considering the ISC/RISC

cycle. Therefore, the primary delayed fluorescence ( $\Phi_{DF1}$ , i.e., primary delayed emission  $\Phi_{DE1}$ ) can be formulated as a function of the radiative fraction to the total efficiency,  $\Phi_r^S + \Phi_{nr}^S$ .

$$\Phi_{DF1} = \Phi_{DE1} = \Phi_{ISC} \Phi_{RISC}^{OE} \frac{\Phi_r^S}{\Phi_r^S + \Phi_{nr}^S} = \Phi_{ISC} \Phi_{RISC}^{OE} \frac{\Phi_r^S}{1 - \Phi_{ISC}}. \quad (S15.23)$$

Similarly, the fraction of T<sub>1</sub> exciton decay event via S<sub>1</sub> ( $\Phi_{ISC} \Phi_{IC}^{OE} \Phi_{RIC}^{OE}$ ) can decay either  $\Phi_r^S$  or  $\Phi_{nr}^S$ , because  $\Phi_{RIC}^{OE}$  is the finally distributed exciton ratio after considering both IC/RIC and ISC/RISC cycles (see Eq. S15.17). Therefore, the secondary delayed fluorescence ( $\Phi_{DF2}$ ) can be formulated as a function of  $\Phi_r^S$  to the  $\Phi_r^S + \Phi_{nr}^S$ .

$$\Phi_{DF2} = \Phi_{DE2} R_{DE2}^{DF2} = \Phi_{ISC} \Phi_{IC}^{OE} \Phi_{RIC}^{OE} \frac{\Phi_r^S}{\Phi_r^S + \Phi_{nr}^S} = \Phi_{ISC} \Phi_{IC}^{OE} \Phi_{RIC}^{OE} \frac{\Phi_r^S}{1 - \Phi_{ISC}}. \quad (S15.24)$$

where  $R_{DE2}^{DF2}$  is a ratio in of secondary delayed fluorescence in secondary delayed emission,  $\Phi_{DF2}/\Phi_{DE2}$ . In the four-state analysis model, the observed lifetime of secondary delayed fluorescence and phosphorescence are exactly the same ( $1/k_{d2}$ ) since they occur from the same origin of the T<sub>1</sub> state. Therefore, both  $\Phi_{DF2}$  and  $\Phi_{Phos}$  contribute to the secondary delayed emission ( $\Phi_{DE2}$ ). The total PL quantum efficiency ( $\Phi_{PLQY}$ ) is the sum of  $\Phi_r^S$ ,  $\Phi_{DF1}$ , and  $\Phi_{DE2}$ . Based on the above analysis, all of the efficiencies related to the TADF process were presented in Eqs. S15.25-S15.32.

$$\Phi_r^S = \frac{k_r^S}{k_r^S + k_{nr}^S + k_{ISC}} = \frac{k_r^S}{k_p}. \quad (S15.25)$$

$$\Phi_{nr}^S = 1 - \Phi_r^S - \Phi_{ISC} = \frac{k_{nr}^S}{k_r^S + k_{nr}^S + k_{ISC}} = \frac{k_{nr}^S}{k_p}. \quad (S15.26)$$

$$\Phi_{ISC} = \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} = \frac{k_{ISC}}{k_p}. \quad (S15.27)$$

$$\Phi_{RISC}^{OE} = \frac{\Phi_{DE1}(1 - \Phi_{ISC})}{\Phi_r^S \Phi_{ISC}} = \frac{(1 - \Phi_{ISC})k_{RISC}}{(1 - \Phi_{ISC})k_{RISC} + k_{IC}} = \frac{(1 - \Phi_{ISC})k_{RISC}}{k_{d1}}. \quad (S15.28)$$

$$\Phi_{IC}^{OE} = \frac{k_{d2}}{k_{RIC}^T} \cdot \frac{\Phi_{DF2}}{\Phi_{DF1}} = \frac{k_{IC}}{(1 - \Phi_{ISC})k_{RISC} + k_{IC}} = 1 - \Phi_{RISC}^{OE}. \quad (S15.29)$$

$$\Phi_{RIC}^{OE} = \frac{\Phi_{RISC}^{OE} k_{RIC}^T}{\Phi_{RISC}^{OE} k_{RIC}^T + k_r^T + k_{nr}^T} = \frac{\Phi_{RISC}^{OE} k_{RIC}^T}{k_{d2}}. \quad (S15.30)$$

$$\Phi_r^{TOE} = \frac{\Phi_{Phos}}{\Phi_{ISC} \Phi_{IC}^{OE}} = \frac{\Phi_{DE2}(1 - R_{DE2}^{DF2})}{\Phi_{ISC} \Phi_{IC}^{OE}} = \frac{k_r^T}{\Phi_{RISC}^{OE} k_{RIC} + k_r^T + k_{nr}^T} = \frac{k_r^T}{k_{d2}}. \quad (S15.31)$$

$$\Phi_{nr}^{TOE} = \frac{1 - \Phi_{PLQY}}{\Phi_{ISC} \Phi_{IC}^{OE}} - \Phi_{nr}^S = \frac{1 - \Phi_{ISC} \Phi_{IC}^{OE} (1 - \Phi_{RIC}^{OE})}{\Phi_{ISC} \Phi_{IC}^{OE} (1 - \Phi_{ISC})} = \frac{k_{nr}^T}{\Phi_{RISC}^{OE} k_{RIC} + k_r^T + k_{nr}^T} = \frac{k_{nr}^T}{k_{d2}}. \quad (S15.32)$$

The corresponding rate constants are described by Eqs. S15.33-S15.40.

$$k_r^S = k_p \Phi_r^S. \quad (S15.33)$$

$$k_{nr}^S = k_p \Phi_{nr}^S = k_p (1 - \Phi_r^S - \Phi_{ISC}). \quad (S15.34)$$

$$k_{ISC} = k_p \Phi_{ISC}. \quad (S15.35)$$

$$k_{RISC} = k_{d1} \frac{\Phi_{RISC}^{OE}}{1 - \Phi_{ISC}} = \frac{k_p k_{d1}}{k_{ISC}} \cdot \frac{\Phi_{DF1}}{\Phi_r^S} = k_{d1} \frac{\Phi_{DF1}}{\Phi_r^S \Phi_{ISC}}. \quad (S15.36)$$

$$k_{IC}^T = k_{d1} - (1 - \Phi_{ISC}) k_{RISC}. \quad (S15.37)$$

$$k_{RIC}^T = k_{d2} \frac{\Phi_{RIC}^{T\ OE}}{\Phi_{RISC}^{T\ OE}} = k_{d2} \frac{(1 - \Phi_{ISC})\Phi_{DE2}R_{DE2}^{DF2}}{\Phi_r^S \Phi_{ISC} \Phi_{RISC}^{OE} \Phi_{IC}^{T\ OE}}. \quad (S15.38)$$

$$k_r^T = k_{d2} \Phi_r^{T\ OE} = k_{d2} \frac{\Phi_{DE2}(1 - R_{DE2}^{DF2})}{\Phi_{ISC} \Phi_{IC}^{T\ OE}}. \quad (S15.39)$$

$$k_{nr}^T = k_{d2} \Phi_{nr}^{T\ OE} = k_{d2} \frac{1 - \Phi_{PLQY}}{\Phi_{ISC} \Phi_{IC}^{T\ OE}} - k_{d2} \Phi_{nr}^S \frac{1 + \Phi_{ISC} \Phi_{IC}^{T\ OE} (\Phi_{RIC}^{T\ OE} - 1)}{\Phi_{ISC} \Phi_{IC}^{T\ OE} (1 - \Phi_{ISC})}. \quad (S15.40)$$

The value of  $R_{DE2}^{DF2}$  can be estimated by fitting the secondary delayed emission spectrum with the prompt fluorescence and phosphorescence spectra to provide the contribution of the phosphorescence to the secondary delayed emission. For the data collected at high temperature,  $R_{DE2}^{DF2}$  can be approximate as 1.

Because we obtained above rate equations by minimum assumptions. We can employ the constraint  $\Phi_{nr}^S = 0$  or  $\Phi_{nr}^T = 0$  as limit conditions to provide the  $\Phi_{ISC}$  values of  $\Phi_{ISC}^{nrS=0}$  and  $\Phi_{ISC}^{nrT=0}$ , respectively, as below.

$$\Phi_{ISC}^{nrS=0} = 1 - \Phi_r^S. \quad (S15.41)$$

$$\Phi_{ISC}^{nrT=0} = \frac{\Phi_{PLQY} - \Phi_r^S - (1 - \Phi_r^S)\Phi_{Phos}}{\Phi_{PLQY} - \Phi_{Phos}} \approx \frac{\Phi_{PLQY} - \Phi_r^S}{\Phi_{PLQY}}, \quad (\because R_{DE2}^{DF2} \approx 1). \quad (S15.42)$$

We can also calculate the average  $k_{ISC}$ ,  $k_{RISC}$ ,  $k_{IC}^T$  and  $k_{RIC}^T$  values with the range between the limit conditions ( $\Phi_{nr}^S = 0$  or  $\Phi_{nr}^T = 0$ ), when it is difficult to estimate  $\Phi_{ISC}$ . By using  $\Phi_{ISC}^{nrS=0}$  and  $\Phi_{ISC}^{nrT=0}$ ,  $\Phi_{RISC}^{nrS=0}$  and  $\Phi_{RISC}^{nrT=0}$  are estimated from Eq. S15.36. The average rate constants for ISC and RISC can be obtained from Eqs. S9.1 and S9.2, respectively. The average rate constants for IC and RIC can be obtained by Eqs. S15.43 and S15.44.

$$k_{IC}^{Avg.} \equiv \frac{(k_{IC}^{nrS=0} + k_{IC}^{nrT=0})}{2} \pm \frac{(k_{IC}^{nrS=0} - k_{IC}^{nrT=0})}{2}. \quad (S15.43)$$

$$k_{RIC}^{Avg.} \equiv \frac{(k_{RIC}^{nrT=0} + k_{RIC}^{nrS=0})}{2} \pm \frac{(k_{RIC}^{nrT=0} - k_{RIC}^{nrS=0})}{2}. \quad (S15.44)$$

When  $\Phi_{Phos}$  is approximated as 0 (i.e.,  $R_{DE2}^{DF2} \approx 1$ ) for the simplification, these average values can be estimated as followed.

$$k_{ISC}^{Avg.} = \frac{k_p [2\Phi_{PLQY} - \Phi_{PF}(1 + \Phi_{PLQY}) \pm \Phi_{PF}(1 - \Phi_{PLQY})]}{2\Phi_{PLQY}}. \quad (S15.45)$$

$$k_{RISC}^{Avg.} = \frac{k_{d1}\Phi_{DF1} [2\Phi_{PLQY} - \Phi_{PF}(1 + \Phi_{PLQY}) \pm \Phi_{PF}(1 - \Phi_{PLQY})]}{2\Phi_{PF}(1 - \Phi_{PF})(\Phi_{PLQY} - \Phi_{PF})}. \quad (S15.46)$$

$$k_{IC}^{Avg.} = k_{d1} - \frac{k_{d1}\Phi_{DF1} [1 + \Phi_{PLQY} - 2\Phi_{PF} \pm (1 - \Phi_{PLQY})]}{2(1 - \Phi_{PF})(\Phi_{PLQY} - \Phi_{PF})}. \quad (S15.47)$$

$$k_{RIC}^{Avg.} = \frac{k_{d2} [2\Phi_{DF2}(1 - \Phi_{PF}) + \Phi_{DF1}(1 - \Phi_{PLQY}) \pm \Phi_{DF1}(1 - \Phi_{PLQY})]}{2\Phi_{DF1}(1 - \Phi_{PF} - \Phi_{DF1})}. \quad (S15.48)$$

## 16. Average and maximum rate equations corrected by exact solution (for Table 2 entry 5)

Comparing Eqs. 59 (with the approximation of no phosphorescence) and 86, the  $k_{ISC}$  have a difference while both equations are same conditions; that means  $k_r^T = 0$  and  $k_{nr}^T = 0$ .

Therefore, the relationship between  $k_{ISC}^{exact}$  and  $k_{ISC}^{nrT=0}$  can be written by

$$k_{ISC}^{exact} = k_{ISC}^{nrT=0} - k_d \frac{\Phi_{DF}}{\Phi_{PF}}, \quad (S16.1)$$

where  $k_{ISC}^{exact}$  is the ISC rate constants in exact solution on three states. This difference is caused by the approximation of  $k_p \approx k^S$ . Therefore,  $k_{ISC}^{nrT=0}$  should be corrected as

$$k_{ISC}^{nrT=0} = k_p \frac{\Phi_{DF}}{\Phi_{PLQY}} - k_d \frac{\Phi_{DF}}{\Phi_{PF}}. \quad (S16.2)$$

When  $k_{nr}^T = 0$ ,  $k_{RISC}$  is maximum value, and the difference of  $k_p$  and  $k^S$  at  $k_{nr}^T = 0$  is also the maximum value of  $k_d \Phi_{DF}/\Phi_{PF}$  (see Eq. 82). On the other hand, while it is difficult to know the difference of  $k_p$  and  $k^S$ ,  $\Phi_{ISC}^{nrS=0}$  should be  $1 - \Phi_{PF}$  when  $k_{nr}^S = 0$ .

Therefore, Eq. S10.1 should be corrected as

$$\begin{aligned} k_{ISC}^{Avg.} &= \frac{1}{2} \left[ k_p(1 - \Phi_{PF}) + k_p \frac{\Phi_{DF}}{\Phi_{PLQY}} - k_d \frac{\Phi_{DF}}{\Phi_{PF}} \right] \pm \frac{1}{2} \left[ k_p(1 - \Phi_{PF}) - \left( k_p \frac{\Phi_{DF}}{\Phi_{PLQY}} - k_d \frac{\Phi_{DF}}{\Phi_{PF}} \right) \right] \\ &= \frac{k_p(1 - \Phi_{PF})\Phi_{PF}\Phi_{PLQY} + (k_p\Phi_{PF} - k_d\Phi_{PLQY})\Phi_{DF} \pm [k_p\Phi_{PF}^2(1 - \Phi_{PLQY}) + k_d\Phi_{DF}\Phi_{PLQY}]}{2\Phi_{PF}\Phi_{PLQY}}. \end{aligned} \quad (S16.3)$$

The maximum values of  $k_{nr}^S$  and  $k_{nr}^T$  should be same with Table 2 entry 4 and Table 2 entry 2, respectively.