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Comprehensive Understanding of Multiple Resonance Thermally Activated Delayed Fluorescence via Quantum Chemistry Calculations

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Abstract

Molecules that exhibit multiple resonance (MR) type thermally activated delayed fluorescence (TADF) are highly efficient electroluminescent materials with narrow emission spectra. Despite their importance in various applications, the emission mechanism is still controversial. Here, a comprehensive understanding of the mechanism for a representative MR-TADF molecule (5,9-diphenyl-5,9-diaza-13b-boranaphtho[3,2,1-*de*]anthracene, DABNA-1) is presented. Using the equation-of-motion coupled-cluster singles and doubles method and Fermi's golden rule, we quantitatively reproduced all rate constants relevant to the emission mechanism; prompt and delayed fluorescence, internal conversion (IC), intersystem crossing, and reverse intersystem crossing (RISC). In addition, the photoluminescence quantum yield and its prompt and delayed contributions were quantified by calculating the population kinetics of excited states and the transient photoluminescence decay curve. The calculations also revealed that TADF occurred via a stepwise process of thermally activated IC from electronically excited T_1 to the second-lowest triplet state, T_2 , RISC from T_2 to S_1 , and fluorescence from S_1 .

Introduction

Since highly efficient thermally activated delayed fluorescence (TADF) was first used in organic light-emitting diodes (OLEDs),¹ many TADF molecules containing various electron donor and acceptor groups have been developed.²⁻⁹ An important factor for TADF efficiency is the energy difference between the lowest triplet state (T_1) and the lowest excited singlet state (S_1), $\Delta E(T_1 \rightarrow S_1)$; a small $\Delta E(T_1 \rightarrow S_1)$ (<200 meV) is required to induce $T_1 \rightarrow S_1$ reverse intersystem crossing (RISC). Another important factor is a large transition dipole moment between S_1 and ground-state S_0 to accelerate the rate of $S_1 \rightarrow S_0$ fluorescence. Experimentally, efficient RISC and high photoluminescence quantum yields (PLQYs) have been simultaneously realized by combining suitable donor and acceptor units that control the spatial overlap between the highest-occupied molecular orbitals (HOMOs) and the lowest-unoccupied molecular orbitals (LUMOs).¹⁻
⁹ It is important to note that the fluorescence spectra were broadened because of the charge-transfer character of S_1 , which was a significant drawback for OLED applications in displays.

In 2016, Hatakeyama et al. developed a new class of TADF molecules.¹⁰ Using a triphenylboron core possessing two nitrogen atoms (5,9-diphenyl-5,9-diaza-13b-boranaphtho[3,2,1-*de*]anthracene, DABNA-1, Fig. 1a), they observed a HOMO-LUMO separation without a conventional donor-acceptor structure, providing efficient TADF with a narrow emission spectrum. The HOMO-LUMO separation resulted from a multiple resonance (MR) effect, that is an opposite resonance effect induced by the boron and nitrogen atoms. MR-TADF molecules emitting blue-to-red fluorescence have been reported.¹¹⁻³⁹

Several theoretical studies have attempted to reveal the TADF mechanism in MR molecules. Northey *et al.* investigated an intersystem-crossing (ISC) mechanism in DABNA-1

using quantum dynamics and time-dependent density-functional theory (TD-DFT) at the PBE0/6-31G(d) level.⁴⁰ There was only a 0.02 eV energy difference between T₂ and S₁, $\Delta E(T_2 \rightarrow S_1)$. However, $\Delta E(T_1 \rightarrow S_1)$ and $\Delta E(T_1 \rightarrow T_2)$ were large, 0.59 eV and 0.61 eV, respectively, which could not explain efficient RISC from T₁ to S₁. Gao *et al.* examined the density-functional dependence of $\Delta E(T_1 \rightarrow S_1)$ within the framework of TD-DFT.⁴¹ The MPWK1CIS functional reproduced the experimental $\Delta E(T_1 \rightarrow S_1)$,⁴¹ as reviewed by Suresh *et al.*²¹ However, the RISC rate constant (k_{RISC}) was not calculated and the TADF mechanism was unclear. Also, they considered TADF in terms of direct (one-step) T₁→S₁ RISC, which differed from the work of Northey *et al.*⁴⁰ Pershin *et al.* reported that TD-DFT methods overestimated $\Delta E(T_1 \rightarrow S_1)$ for MR molecules, and that the spin-component-scaling second-order approximate coupled-cluster (SCS-CC2) method outperformed TD-DFT for predicting $\Delta E(T_1 \rightarrow S_1)$.^{42,43} The partial inclusion of double excitations within the SCS-CC2 method was responsible for the improved accuracy in predicting $\Delta E(T_1 \rightarrow S_1)$. The SCS-CC2 calculation of DABNA-1-based molecules revealed the relationship between its molecular structure and electronic properties, $\Delta E(T_1 \rightarrow S_1)$, and the fluorescence rate constant. However, the TADF mechanism was still unclear because the k_{RISC} was not calculated. Lin *et al.* calculated rate constants for fluorescence (k_{F}), ISC (k_{ISC}), k_{RISC} , and internal conversion (IC) (k_{IC}) for DABNA-1.⁴⁴ However, the calculated k_{RISC} was $6.7 \times 10^2 \text{ (s}^{-1}\text{)}$, which was much less than the experimental value of $1.0 \times 10^4 \text{ s}^{-1}$.¹⁰ The calculated k_{ISC} of $1.4 \times 10^4 \text{ (s}^{-1}\text{)}$ was two orders of magnitude less than the experimental value of $4.5 \times 10^6 \text{ s}^{-1}$.¹⁰ In addition, the calculated non-radiative decay, $k_{\text{IC}}(S_1 \rightarrow S_0)$, was greater than the $k_{\text{F}}(S_1 \rightarrow S_0)$, suggesting that the PLQY of DABNA-1 was less than 50%, in contrast with the 88% experimental value.¹⁰ All these previous studies⁴⁰⁻⁴⁴ only partially explained the photophysical properties of MR-TADF mainly because crucial RISC was not elucidated.

Here, we report a comprehensive understanding of the TADF mechanism using the representative MR molecule, DABNA-1. So far, $\Delta E(T_1 \rightarrow S_1)$ (and spin-orbit coupling (SOC) in some cases) and oscillator strength have been considered to understand the TADF mechanism and to design TADF molecules. However, these are not sufficient for the above aim; quantifications of all types of rate constants and those of energy levels including higher-lying states relevant to the emission process are required for the complete understanding of the emission mechanism. Recently, we reported rate-constant predictions enabled by a proposed cost-effective calculation method based on Fermi's golden rule.⁴⁵ Using the method, we calculated k_{IC} , k_{ISC} , k_{RISC} , k_F , and the rate constant for phosphorescence (k_{Phos}), of benzophenone as an example. The calculated rate constants agreed well with experimental values. Here, we applied the same method to DABNA-1 and determined all relevant rate constants. We also determined the lifetime of the delayed component in transient PL (trPL), the rate constant of TADF (k_{TADF}) and the PLQY, by calculating the population kinetics of the excited states and the trPL decay curve. The calculations also indicated that, after photoexcitation, T_1 was first generated via $S_1 \rightarrow T_2$ ISC and $T_2 \rightarrow T_1$ IC. Then, triplet-to-singlet conversion occurred via thermally activated $T_1 \rightarrow T_2$ IC and $T_2 \rightarrow S_1$ RISC.

Results

Calculation of matrix elements between vibronic states. Geometry optimization and frequency analysis of S_0 for DABNA-1 were performed using the TPSSh/6-31+G(d) method, whereas those of S_1 , T_1 , and T_2 were performed using the TD-TPSSh/6-31+G(d) method. The polarizable continuum model (PCM) of a CH_2Cl_2 solvent was used to consider the effects on

vibronic states. We used the functional and the PCM conditions for ground- and excited-state geometry optimizations because Gao *et al.* reported that the TPSSh/6-31+G(d)-PCM model reproduced experimental DABNA-1 emission and absorption wavelengths in CH₂Cl₂.⁴¹ Geometry optimization and frequency analysis were performed with the Gaussian 16 program package.⁴⁶ For MR molecules, the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method and algebraic diagrammatic construction of the second order, have been shown to be suitable for calculating singlet-triplet energy differences.^{42,47-49} Here, excited-state calculations were performed using the EOM-CCSD/6-31G method implemented in the Q-Chem program package.⁵⁰

Excitation energies, SOCs, vibronic couplings, transition-dipole moments, and permanent dipole moments were calculated using EOM-CCSD wave functions. At the TD-TPSSh level, S₁ and T₁ local-energy minima were located at the S₁ and T₁ optimized geometries, respectively. However, as shown in Supplementary Table 12 and Supplementary Fig. 3, the lowest S₁ and T₁ energy levels calculated at the EOM-CCSD level were both located at the T₁ geometry (3.37 and 3.18 eV, respectively). In addition, the S₁ and T₁ structures were nearly the same including the dihedral angles (Supplementary Table 5); hence, the structure was denoted the S₁T₁ geometry. Because the Stokes shift was experimentally observed for DABNA-1 in solution and in solid films,¹⁰ it was reasonably assumed that the initial TADF state was the S₁ adiabatic energy minimum. The S₀, S₁, T₁, and T₂ electronic states and the S₁T₁ and T₂ equilibrium geometries were used to model TADF for DABNA-1 (eight electronic states in all). Because S₂ states were 0.89 eV higher in energy than the S₁ states, their contributions were neglected (Supplementary Fig. 3). The T₃ states were 0.2 eV higher than S₁, but were neglected because the electronic-transition rate constants from S₁ to T₃ were far smaller than those of the competing processes (S₁

to T₁ and S₁ to T₂) and that from T₂ to T₃ was smaller than that from T₂ to T₁ (Supplementary Fig. 3). In the EOM-CCSD calculations, S₁ and T₁ involved predominantly HOMO→LUMO transitions, whereas T₂ involved predominantly a linear combination of HOMO→LUMO+5 and HOMO−1→LUMO transitions (Fig. 1a, Supplementary Tables 6–9). Figure 1b shows a calculated energy-level diagram of DABNA-1. The adiabatic T₁→S₁ energy difference calculated with the EOM-CCSD/6-31G(d) method (S₁T₁ geometry) was only 0.06 eV larger than the experimentally obtained 0.2 eV. Thus, EOM-CCSD significantly improved the overestimation of $\Delta E(T_1 \rightarrow S_1)$, relative to those by previously reported TD-DFT methods.^{40,42–44}

Calculation of rate constants and luminescence quantum efficiencies. We examined triplet formation from S₁. Figure 1b shows calculated energy differences and SOCs, and Table 1 lists calculated and experimental values of k_{IC} , k_{ISC} , k_{RISC} , k_F , and k_{Phos} . The raw rate constants in Table 1 were calculated using excitation energies calculated via EOM-CCSD. (Corrected values are discussed below.) We evaluated the consistency between the raw and experimental rate constants. Equations for k_{IC} , k_{ISC} , k_{RISC} , k_F , and k_{Phos} are given in the Supplementary Information (Supplementary Equations S1–S9).

Calculated values of $k_F(S_1 \rightarrow S_0)$ ($1.4 \times 10^8 \text{ s}^{-1}$) and $k_{IC}(S_1 \rightarrow S_0)$ ($1.2 \times 10^7 \text{ s}^{-1}$) agreed quantitatively with experimental results ($1.0 \times 10^8 \text{ s}^{-1}$ and $1.3 \times 10^7 \text{ s}^{-1}$, respectively) determined by Hatakeyama *et al.*¹⁰ from PL decay curves of a 1-wt% DABNA-1: 9,9'-biphenyl-3,3'-diylbis-9H-carbazole film at 300 K (Table 1). The experimentally obtained k_{ISC} value ($4.5 \times 10^6 \text{ s}^{-1}$) agreed with $k_{ISC}(S_1 \rightarrow T_2)$ ($5.4 \times 10^6 \text{ s}^{-1}$), rather than $k_{ISC}(S_1 \rightarrow T_1)$ ($1.7 \times 10^5 \text{ s}^{-1}$), suggesting that the experimental k_{ISC} should be assigned to $k_{ISC}(S_1 \rightarrow T_2)$. The $k_{ISC}(S_1 \rightarrow T_2)$ was ten times greater than $k_{ISC}(S_1 \rightarrow T_1)$, because of the larger S₁-T₂ SOC (1.52 cm^{-1}) relative to that of S₁-T₁ (0.06 cm^{-1}). The large S₁→T₂ SOC enhanced S₁→T₂ ISC, despite the uphill transition from S₁ to T₂ (the

Franck-Condon energy difference was 135 meV, Fig. 1b), compared with the downhill transition from S_1 to T_1 (260 meV). The small S_1 - T_1 SOC resulted from very similar S_1 and T_1 orbital configurations (HOMO→LUMO transition). These results suggested that the ISC (S_1 → T_1 conversion) of DABNA-1 occurred via the stepwise S_1 → T_2 → T_1 process, rather than by the one-step S_1 → T_1 ISC, irrespective of the geometry relaxation (gray arrows in Fig. 1c). Such T_2 -supported ISC is experimentally observed for a TADF system when $\Delta E(S_1$ → $T_2)$ is sufficiently small.⁵¹ Because T_2 → T_1 IC was much faster than S_1 → T_2 ISC, the latter was the rate determining step of the S_1 → T_2 → T_1 process (Fig. 1c). Hence, the net rate constant $k(S_1$ → T_2 → $T_1)$ was approximately equal to $k_{ISC}(S_1$ → $T_2) = 5.4 \times 10^6 \text{ s}^{-1}$ (Table 1).

For RISC from T_1 , the calculated $k_{RISC}(T_1$ → $S_1)$ (2.5 s^{-1}) was considerably less than the experimental value ($1 \times 10^4 \text{ s}^{-1}$),¹⁰ indicating that T_1 → S_1 conversion did not occur in one-step but via a more effective process. Because the S_2 and T_3 energy levels, as well as higher singlet and triplet states, could not contribute to the RISC from T_1 , as discussed above, and T_2 was close to S_1 (see Supplementary Fig. 3), stepwise T_1 → T_2 → S_1 was the most promising mechanism (green arrows in Fig. 1c). To determine $k(T_1$ → T_2 → $S_1)$, we calculated the trPL decay curve (Fig. 2) via kinetic equations (Supplementary Equations S10 – S17 and Supplementary Table 15). The total PLQY (Φ) and the TADF lifetime (τ_{TADF}) were then obtained from the trPL decay curve (Fig. 2). The prompt and delayed components of Φ (Φ_P and Φ_{TADF} , respectively) were calculated from:

$$\Phi_P = \frac{k_F(S_1 \rightarrow S_0)}{k_F(S_1 \rightarrow S_0) + k_{IC}(S_1 \rightarrow S_0) + k_{ISC}(S_1 \rightarrow T_2) + k_{ISC}(S_1 \rightarrow T_1)} \quad (1)$$

$$\Phi_{TADF} = \Phi - \Phi_P \quad (2)$$

and the ISC quantum yield (Φ_{ISC}) was calculated from:

$$\Phi_{ISC} = \frac{k_{ISC}(S_1 \rightarrow T_2) + k_{ISC}(S_1 \rightarrow T_1)}{k_F(S_1 \rightarrow S_0) + k_{IC}(S_1 \rightarrow S_0) + k_{ISC}(S_1 \rightarrow T_2) + k_{ISC}(S_1 \rightarrow T_1)} \quad (3)$$

Then, k_{TADF} was determined from:¹⁰

$$k_{\text{TADF}} = \frac{\Phi_{\text{TADF}}}{\Phi_{\text{ISC}}\tau_{\text{TADF}}} \quad (4)$$

Finally, $k(\text{T}_1 \rightarrow \text{T}_2 \rightarrow \text{S}_1)$ was calculated from:

$$k(\text{T}_1 \rightarrow \text{T}_2 \rightarrow \text{S}_1) = \frac{k_{\text{F}}(\text{S}_1 \rightarrow \text{S}_0) \times k_{\text{TADF}}}{k_{\text{F}}(\text{S}_1 \rightarrow \text{S}_0) - k(\text{S}_1 \rightarrow \text{T}_2 \rightarrow \text{T}_1)} \quad (5)$$

Table 1 also lists calculated Φ , Φ_{P} , Φ_{TADF} , Φ_{ISC} , τ_{TADF} , k_{TADF} , $k(\text{T}_1 \rightarrow \text{T}_2 \rightarrow \text{S}_1)$, and $k(\text{S}_1 \rightarrow \text{T}_2 \rightarrow \text{T}_1)$ values. The Φ , Φ_{P} , Φ_{TADF} , and Φ_{ISC} values were quantitatively consistent with the experimental values because of the quantitative predictions for $k_{\text{F}}(\text{S}_1 \rightarrow \text{S}_0)$, $k_{\text{IC}}(\text{S}_1 \rightarrow \text{S}_0)$, $k_{\text{ISC}}(\text{S}_1 \rightarrow \text{T}_2)$, and $k_{\text{ISC}}(\text{S}_1 \rightarrow \text{T}_1)$. The calculated conversion rate constant $k(\text{S}_1 \rightarrow \text{T}_2 \rightarrow \text{T}_1)$ was consistent with the experimental k_{ISC} , suggesting that the experimental ISC should be assigned to $\text{S}_1 \rightarrow \text{T}_2 \rightarrow \text{T}_1$ ISC rather than direct $\text{S}_1 \rightarrow \text{T}_1$ ISC. All the calculated single step rate constants and $k(\text{S}_1 \rightarrow \text{T}_2 \rightarrow \text{T}_1)$ agreed well with the experimental values. However, the agreements of the calculated k_{TADF} and $k(\text{T}_1 \rightarrow \text{T}_2 \rightarrow \text{S}_1)$ ($0.16 \times 10^4 \text{ s}^{-1}$ and $0.17 \times 10^4 \text{ s}^{-1}$, respectively) and the experiments ($0.94 \times 10^4 \text{ s}^{-1}$ and $1.0 \times 10^4 \text{ s}^{-1}$, respectively) were not as good as we expected, compared to the case of $k(\text{S}_1 \rightarrow \text{T}_2 \rightarrow \text{T}_1)$. Considering that they included the uphill-energy $\text{T}_1 \rightarrow \text{T}_2$ IC, there was a possibility that $\Delta E(\text{T}_1 \rightarrow \text{T}_2)$ was overestimated, leading to an underestimation of $k_{\text{IC}}(\text{T}_1 \rightarrow \text{T}_2)$, k_{TADF} , and $k(\text{T}_1 \rightarrow \text{T}_2 \rightarrow \text{S}_1)$.

To examine the effect of $\Delta E(\text{T}_1 \rightarrow \text{T}_2)$ on $k_{\text{IC}}(\text{T}_1 \rightarrow \text{T}_2)$, k_{TADF} , and $k(\text{T}_1 \rightarrow \text{T}_2 \rightarrow \text{S}_1)$, we recalculated these rate constants using a corrected $\Delta E(\text{T}_1 \rightarrow \text{T}_2)$. The rate-determining step for the T_2 -mediated RISC was $\text{T}_1 \rightarrow \text{T}_2$ IC; hence, $\Delta E(\text{T}_1 \rightarrow \text{T}_2)$ could be viewed as the activation energy for DABNA-1 TADF and RISC. As discussed above, the energy difference between the calculated and experimental $\text{T}_1 \rightarrow \text{S}_1$ was 60 meV. Thus, 60 meV was subtracted from the EOM-CCSD-calculated $\Delta E(\text{T}_1 \rightarrow \text{T}_2)$ value of 252 meV. The energy-levels and rate constants calculated

with the corrected $\Delta E(T_1 \rightarrow T_2)$ are also listed in Table 1. The value of $k(S_1 \rightarrow T_2 \rightarrow T_1)$ was unchanged, suggesting that the T_1 energy correction had little effect on the ISC. In contrast, $k_{IC}(T_1 \rightarrow T_2)$ increased from $1.1 \times 10^7 \text{ s}^{-1}$ to $3.3 \times 10^8 \text{ s}^{-1}$. As a result, k_{TADF} and $k(T_1 \rightarrow T_2 \rightarrow S_1)$ increased to $1.8 \times 10^4 \text{ s}^{-1}$ and $1.9 \times 10^4 \text{ s}^{-1}$, respectively, which were in much better agreements with the experiments. These results suggested that the $\Delta E(T_1 \rightarrow T_2)$ overestimation was responsible for the underestimation of k_{TADF} and $k(T_1 \rightarrow T_2 \rightarrow S_1)$. Thus, k_{TADF} and $k(T_1 \rightarrow T_2 \rightarrow S_1)$ depended largely on $k_{IC}(T_1 \rightarrow T_2)$, which was the sum of IC rate constants for individual molecular vibrations, $k_{IC,\alpha}(T_1 \rightarrow T_2)$, where α denoted the α th vibrational mode (Supplementary Equations S5-S7). A combined in-plane and out-of-plane bending mode (743 cm^{-1}) had the largest $k_{IC,\alpha}(T_1 \rightarrow T_2)$ value (Supplementary Table 14 and Supplementary Fig. 5), suggesting that the $T_1 \rightarrow T_2$ IC was predominantly accelerated by the bending mode.

Discussion

In this work, we calculated the IC, ISC, RISC, fluorescence, phosphorescence, and TADF rate constants for DABNA-1, using EOM-CCSD wave functions and Fermi's golden rule. The values quantitatively reproduced those from experiments, and thus validated the calculations. Various quantum yields, including PLQY, were also predicted and we revealed the DABNA-1 decay mechanism. The calculated population kinetics and the trPL decay curve indicated that TADF from DABNA-1 occurs via consecutive two processes, $T_1 \rightarrow T_2$ IC and $T_2 \rightarrow S_1$ RISC. Our proposed method here will be useful for accurate prediction of all rate constants and quantum yields relevant to OLED phenomena for various compounds with a wide range of structures in future.

Fig. 1 Molecular orbitals and electronic transitions of DABNA-1. **a** Structure of DABNA-1 and HOMO-1, HOMO, LUMO, and LUMO+5 distributions calculated at the RHF/6-31G level (HOMO = highest-occupied molecular orbital, LUMO = lowest-unoccupied molecular orbital). **b** Energy differences (meV) between S_1 , T_1 , and T_2 . S_1 - T_1 and S_1 - T_2 spin-orbit couplings (cm^{-1}). **c** The stepwise $S_1 \rightarrow T_2 \rightarrow T_1$ and $T_1 \rightarrow T_2 \rightarrow S_1$ processes of DABNA-1. The grey solid arrow depicts stepwise $S_1 \rightarrow T_2 \rightarrow T_1$; the green solid arrow depicts stepwise $T_1 \rightarrow T_2 \rightarrow S_1$; the dotted arrows show minor decay and up-conversion processes. The values are calculated rate constants for one-

step transitions. **d** The energy differences calculated using the corrected T_1 energy. **e** Calculated rate constants for one-step transitions using the corrected T_1 energy.

Fig. 2 Calculated transient photoluminescence (trPL) decay curve. The inset is a log-log plot of the decay curve.

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Author Contributions

K.S. performed the theoretical calculations. H.K. planned and supervised the project. All authors contributed to the writing of this manuscript and have approved the final version.

Competing Interests

The authors have no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at https://***

Figure Legends and Tables

Fig. 1 Molecular orbitals and electronic transitions of DABNA-1. **a** Structure of DABNA-1 and HOMO-1, HOMO, LUMO, and LUMO+5 distributions calculated at the RHF/6-31G level (HOMO = highest-occupied molecular orbital, LUMO = lowest-unoccupied molecular orbital). **b** Energy differences (meV) between S₁, T₁, and T₂. S₁-T₁ and S₁-T₂ spin-orbit couplings (cm⁻¹). **c** The stepwise S₁→T₂→T₁ and T₁→T₂→S₁ processes of DABNA-1. The grey solid arrow depicts stepwise S₁→T₂→T₁; the green solid arrow depicts stepwise T₁→T₂→S₁; the dotted arrows show minor decay and up-conversion processes. The values are calculated rate constants for one-step transitions. **d** The energy differences calculated using the corrected T₁ energy. **e** Calculated rate constants for one-step transitions using the corrected T₁ energy.

Fig. 2 Calculated transient photoluminescence (trPL) decay curve. The inset is a log-log plot of the decay curve.

Table 1 Calculated and experimental photophysical properties of DABNA-1. Experimental values are from Hatakeyama et al.¹⁰

	Calc.		Expt.
	Raw [*]	Corrected ^{**}	
$\Delta E(T_1 \rightarrow S_1)$	240	180	
$\Delta E(T_2 \rightarrow S_1)$	-12	-12	
$\Delta E(T_1 \rightarrow T_2)$	252	192	196
$k_F(S_1 \rightarrow S_0)$	$1.4 \times 10^8 \text{ s}^{-1}$	$1.4 \times 10^8 \text{ s}^{-1}$	$1.0 \times 10^8 \text{ s}^{-1}$
$k_{IC}(S_1 \rightarrow S_0)$	$1.2 \times 10^7 \text{ s}^{-1}$	$1.2 \times 10^7 \text{ s}^{-1}$	$1.3 \times 10^7 \text{ s}^{-1}$
$k_{ISC}(S_1 \rightarrow T_1)$	$1.7 \times 10^5 \text{ s}^{-1}$	$2.8 \times 10^5 \text{ s}^{-1}$	
$k_{ISC}(S_1 \rightarrow T_2)$	$5.4 \times 10^6 \text{ s}^{-1}$	$5.4 \times 10^6 \text{ s}^{-1}$	
$k_{IC}(T_2 \rightarrow T_1)$	$1.8 \times 10^{11} \text{ s}^{-1}$	$5.6 \times 10^{11} \text{ s}^{-1}$	
$k_{RISC}(T_2 \rightarrow S_1)$	$2.9 \times 10^8 \text{ s}^{-1}$	$2.9 \times 10^8 \text{ s}^{-1}$	
$k_{Phos}(T_1 \rightarrow S_0)$	$9.4 \times 10^{-1} \text{ s}^{-1}$	$1.9 \times 10^{-1} \text{ s}^{-1}$	
$k_{IC}(T_1 \rightarrow T_2)$	$1.1 \times 10^7 \text{ s}^{-1}$	$3.3 \times 10^8 \text{ s}^{-1}$	
$k_{RISC}(T_1 \rightarrow S_1)$	2.5 s^{-1}	$4.2 \times 10^1 \text{ s}^{-1}$	
Φ	0.92	0.92	0.88
Φ_p	0.89	0.89	0.85
Φ_{TADF}	2.9×10^{-2}	3.2×10^{-2}	3.5×10^{-2}
Φ_{ISC}	3.5×10^{-2}	3.5×10^{-2}	4.0×10^{-2}
τ_{TADF}	$5.2 \times 10^{-4} \text{ s}$	$5.1 \times 10^{-5} \text{ s}$	$9.4 \times 10^{-5} \text{ s}$
k_{TADF}	$0.16 \times 10^4 \text{ s}^{-1}$	$1.8 \times 10^4 \text{ s}^{-1}$	$0.94 \times 10^4 \text{ s}^{-1}$
$k(T_1 \rightarrow T_2 \rightarrow S_1)$	$0.17 \times 10^4 \text{ s}^{-1}$	$1.9 \times 10^4 \text{ s}^{-1}$	$1.0 \times 10^4 \text{ s}^{-1}$
$k(S_1 \rightarrow T_2 \rightarrow T_1)$	$5.4 \times 10^6 \text{ s}^{-1}$	$5.4 \times 10^6 \text{ s}^{-1}$	$4.5 \times 10^6 \text{ s}^{-1}$

^{*}) Energy differences were calculated using the EOM-CCSD/6-31G(d) method (Fig. 1b,c).

^{**}) Corrected energy differences were used (Fig. 1d,e).

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